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# Synergistic influence of micro-nano silica mixture on durability performance of cementious materials

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## HIGHLIGHTS

- Mixing micro-nano silica remarkably enhanced concrete durability than separate use.
- Durability improvement was due to reduced water and chloride ion penetrability.
- Dispersion is one of the key factors controlling micro-nano synergistic efficiency.
- Sensitivity study is recommended for selecting optimum micro-nano mixing ratio.

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## ABSTRACT

Although works have been carried out to explore the influence of adding micro silica (MS) and nano silica (NS) mixture on the main characteristics of cementious materials, the synergistic role of micro-nano silica mixture was rarely studied on the direct corrosion protection performance of concrete. This research is to investigate the efficiency of using MS and NS mixture, as cement partial replacement, on corrosion protection and sulphate resistance of cementious materials. In addition, the influence of this silica multi-sized mixture was also studied on some durability characteristics related to corrosion and sulphate protection. Based on the maximum mortar compressive strength, 10% MS and 2% NS were the optimum cement replacement ratios for each size separately. For the comparative purposes, the total cement replacement ratio of MS and NS mixture was kept equal to the optimum MS (i.e.10%) and hence the optimum mixing ratios for combining MS and NS in a mixture were equal 8% and 2% respectively. Concrete corrosion protection and mortar sulphate resistance were remarkably enhanced by using 2%NS + 8%MS mixture, instead of the optimum MS or NS cement replacement ratios. Further sensitivity study is recommended for the proposed MS + NS mixture considering more controlling factors.



## 1. Introduction

Pozzolanic material is a siliceous or alumino-siliceous fine material that, in the presence of moisture, chemically reacts with the calcium hydroxide $Ca(OH)_2$ or (CH) released by the hydration of Portland cement forming calcium-silicate-hydrate or (C-S-H) [1]. On the other hand, the addition of pozzolanic materials finer than cement can reduce the porosity of cement paste. Silica fume (SF) is a pozzolanic by-product of reducing the high-purity quartz with coal in an electric arc furnace during the manufacture of silicon or ferrosilicon alloy [2]. It is widely recognized that using optimum cement partial replacement ratio of SF increases significantly the durability performance of cement based materials [2]. Perraton et al. [3] concluded that, using 10% SF – as a partial replacement – significantly reduced the chloride-ion permeability of concrete specimens. Khalifa et al. [4] found that using optimum ratio of SF (i.e. 10%), as Portland cement partial replacement, remarkably improved the concrete specimen's water permeability and chloride ion penetrability.

The huge specific surface area of nano-size silica particles enhances their chemical activity, as pozzolanic material [5]. Moreover the reduced size of nano particles permits the quantum effects (i.e. quantum sized pores and tunnels) to play a remarkable role in

*Abbreviations:* CEM I, Ordinary Portland cement according to EN 197-1; CH, Calcium Hydroxide; C-S-H, Calcium Silicate Hydrate; MS, Micro silica fume particles; NS, Nano silica particles; SEM, Scanning Electronic Microscopy; SP, Superplasticizer admixture; TEM, Transmission Electron Microscope; XRD, X-ray Diffraction.

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the particle's surface reactivity and hence in enhancing the cementious materials properties [6,7]. Accordingly, high microstructural density is usually observed in the nano silica modified cementious materials due to either the nano particle's high pozzolanic reactivity or their pore filling mechanism. Therefore, nano silica particles partial replacement enhances strength and durability of cementious materials. On the other hand, nano silica (NS) can also react with CH crystals, arrayed in the interfacial transition zone between hardened cement paste and aggregates, producing more C-S-H gel at this critical bonding zone [8]. Hence, using NS particles instead of micro silica enhances the rate of pozzolanic reactivity and increases the cementitious material's rate of strength gain [8]. Quercia et al. [9] observed that the water permeability was reduced significantly by using 3.8% NS as cement partial replacement in concrete. Based on Scanning Electronic Microscopy (SEM) results, Li et al. [10] and Zaki et al. [11] concluded that using NS enhanced the texture of the cement's hydrate products with a reduction of calcium hydroxide (CH) and increment on the calcium silicate hydrate (C-S-H) ratios. Bianchi et al. [12] presented a comprehensive review on some effects of NS on the durability of concrete. However, Bianchi et al. recommended that further investigations on corrosion resistance and sulphate resistance have to be assessed.

Using high cement replacement ratio of the ultra high surface area of NS may lead to particles agglomeration. Accordingly, the recommended nano replacement ratio – found in literature- is not more than 4%, otherwise either reduction in the cementitious material overall performance is expected or special dispersion processes need to be used. Another drawback, of using high ratio of NS in concrete, is that distributing huge surface area can lead to plastic shrinkage cracks [8,13]. In order to provide efficient use of the nano and micro silica advantages and to avoid some drawbacks, Sakshi [14] suggested that using optimum ratio of combined micro-nano silica particles may create more strong and durable cementitious materials.

Jalal et al. 2012 [15] and Puentes et al. [16] reported the enhancement of some mechanical, durability characteristics (e.g. porosity and permeability) and microstructure properties for high performance self compacting concrete (HPSCC) made of combined micro-silica (MS) and nano-silica (NS). Puentes et al. [16] observed that adding nano silica to SCC provided lower hardened porosity and water vapor permeability, due to the pozzolanic particle size effects. Li et al. [17] observed that the combining MS and NS particles had significant synergistic effect on strength and microstructure of mortar. Similarly, Singh and Dhillon [18] suggested that the MS and NS particles can be added together to achieve higher concrete strength using high range water reducing Superplasticizer to compensate workability. Hendi et al. [19] revealed, using thermogravimetric analysis (TGA), that combination of MS and NS particles boosted calcium hydroxide consumption and provided higher sulfuric acid resistance. Ghafoori et al. [20] found that agglomeration of the fine sized particles -during mixing- negated the expected high sulphate resistance of Portland cement mortar, due to superior pozzolanic activity of combining nano to micro silica.

Efficiency of mixing MS and NS was less explored, in literature, compared to MS or NS separately for the direct durability performance of concrete (e.g. corrosion protection). In this research work, durability influence of using micro-nano silica mixture, as cement partial replacement, was investigated. Concrete corrosion protection and mortar sulphate resistance; were the targeted durability performances. Main corresponding durability characteristics were also investigated such as concrete water permeability and chloride ions penetrability. Sensitivity study was initially implemented to evaluate the efficiency of the available nano particles dispersion systems. Two different techniques were used to dispense the nano silica particles in water to form nano-silica suspension. The efficiency of each technique was evaluated according to the strength progress and variation for 24 mortar specimens, at 4 different ages till 56 days [21]. Special arrangement, for using both techniques, was implemented to achieve better dispersing results.

Initial study was performed to obtain the optimum cement replacement ratio, of either MS or NS particles based on the mortar maximum compressive strength at 56 days. The optimum separate replacement ratios were 10% and 2% for MS or NS particles respectively. These replacement ratios were commonly suggested in literature to enhance the cementitious material's strength and durability performances [3,15]. To assure no conflict occurred due to changing total silica ratio, the total replacement ratio of using MS and NS mixture was kept equal to the optimum measured replacement ratio of the MS (i.e.10%). Having 10% total silica replacement ratio, optimum MS and NS mixing ratios were 8% and 2% respectively, as determined by additional parametric study. Durability influence of the proposed 2%NS + 8%MS mixture was compared with the cases of using either the optimum cement replacement ratios of MS (10%) or NS (2%). Corrosion protection and sulphate resistance were investigated, as both representing main durability performances of cementitious materials. In addition, concrete rapid chloride penetrability, water penetrability and sorptivity were also measured as these durability characteristics are influencing corrosion and sulphate protections. As the nano-micro particles mixing ratio is highly sensitive to silica properties and dispersion of nano particles, guidelines for determining and implementing the optimum MS + NS mixing ratio, are proposed for any further study.

## 2. Materials and test methods

### 2.1. Materials

Cement (CEM I 42.5 N) – complied with EN 197-1 [22] – was used for all mortar and concrete specimens. Densified or MS (i.e. Rheomac SF 100), complied with ASTM C 1240 [23], and NS particles were used as pozzolanic materials. Figs. 1 and 2 show the Transmission Electron Microscope (TEM) and X-ray Diffraction (XRD) pattern of Nano Silica sample -respectively -as provided by the manufacturer. Fig. 1 indicates that the nano particle size range is 8–20 nm and Fig. 2 shows the amorphous nature of NS particles.

Mortar specimens and concrete specimens were made of quartz sand -as fine aggregate- had less than 3% of particles finer than 75 μm which may have negative impact on the pozzolanic activity of nano-size particles. Fine aggregate, complied with ASTM C33 [24]

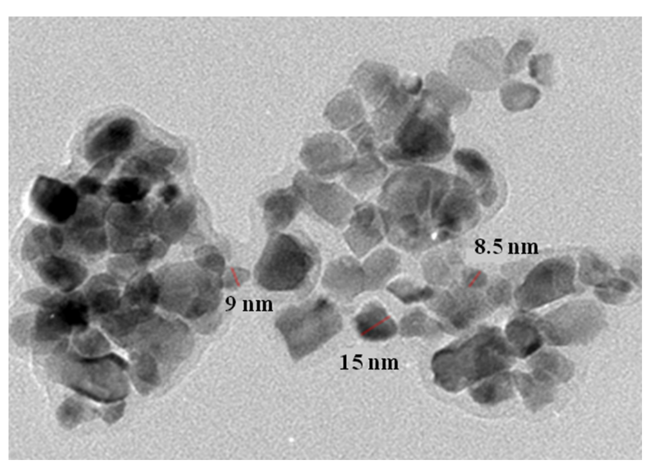


**Fig. 1.** TEM image of Nano Silica particles.