CHARACTERIZATION OF SILICA NANOPARTICLES AND THEIR EFFECT ON MECHANICAL PROPERTIES OF CEMENT PORTLAND 30R.

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ABSTRACT
Cement slurries have been modified with different agents in order to enhance the puzzolanic reaction and increase the calcium silicate hydrate (C-S-H gel) content and therefore, increase their mechanical properties. In particular, nanosilica (NS) particles have been widely used since besides they promote C-S-H gel generation; also prevent pores formation in final cement morphology. In this work NS synthetized by sol-gel method are kept in sol phase in order to preserve the particles dispersion, and then were mixed with cement Portland 30R (CPC 30). Effect of NS content in morphology and mechanical properties of slurries was studied. Optimal NS content was established for the cement slurries formulated according to ASTM standards.

Keywords: nanosilica; dispersion; mechanical properties; cement slurries; hydrosol.

CARACTERIZACION DE NANOPARTICULAS DE SILICE Y SU EFECTO EN LAS PROPIEDADES MECANICAS DE CEMENTO PORTLAND 30R.

RESUMEN
Las formulaciones de lechadas para cementos se han modificado con diferentes agentes con la finalidad de promover la reacción puzolánica e incrementar la cantidad de silicato de calcio hidratado (gel C-S-H) y por lo tanto, las propiedades mecánicas de las mismas. Las partículas de nanosílice (NS), han sido ampliamente utilizadas para este fin ya que además de incrementar el contenido de gel C-S-H, también contribuyen a evitar la formación de poros en la morfología del cemento. En este trabajo, NS sintetizadas por el método sol-gel son mantenidas en la fase sol para preservar la dispersión de partículas, y se mezclaron en diferentes cantidades con cemento Portland 30R (CPC30). Se estudió el efecto del contenido de NS en la morfología y propiedades mecánicas de las lechadas cementantes. Se estableció un contenido óptimo de NS para lechadas formuladas de acuerdo con estándares ASTM.

Palabras clave: Nanosílice, dispersión, propiedades mecánicas, lechadas de cemento, hidrosol.

INTRODUCTION

Concretes are formed by particles of cement, aggregates and water. Reaction between cement and water forms calcium silicate hydrate (C-S-H) gel, which gives it resistance and other mechanical properties, such as chemical resistance and durability; these particles are also affected by the mixing grade and precursors particle sizes distribution. During this hydration reaction, also Portlandite (calcium hydroxide) is generated as byproduct, that does not have any cementitious properties and which is prone to leaching and sulfate attack [1-2].

Addition of puzzolanic materials in different ways such as fly ash, blast furnace slags, silica fume, increase the cement properties, since silica reacts with Portlandite forming additional calcium silicate hydrate (C-S-H) and reducing pore sizes. Recent studies have demonstrated that silica in nanometric sizes, known as Nanosilica (NS), enhances the puzzolanic reaction and the pore filling effect in concretes [1-5]. Several ways of generating NS has been studied, like sol-gel, vaporization, precipitation, biological methods, etc. In this work, a modified sol-gel method was used to produce NS that were added to cement Portland 30R (CPC) in order to investigate the effect of NS particles content on its mechanical properties.

MATERIALS AND METHODS

NS were synthetized by sol-gel method using a non-ionic surfactant agent (Titron X100). Sodium silicate and nitric acid were used as precursors [2]. The systems were forced to remain in sol phase (hydrosol) in order to keep the particles well dispersed. These particles were characterized by TEM, using a FEI Titan 80-300 microscope, to determine their morphology and size distribution. Sample was prepared by diluting 30 µl of the NS sol phase in 250 µl of acetone. This dilution was then sonificated by 30 minutes. After that a drop was deposited on a cupper grid coated with Lacey carbon film. A Nicolet Magna 500 spectrometer was used to obtain the NS chemical composition. Mixtures of CPC 30R and NS were made according to standards ASTM-109M [6] and ASTM-348 [7] in order to respect the maximum water content indicated in them. NS was added in the following contents: 3, 1, 0.5, 0.1, 0.25, 0.01, 0.0075 and 0.001 %. Cubes and bars of 125 cm^3 and 2.54 X 2.54 X 12.7 cm respectively, were prepared with these blends in order to evaluate compressive and flexural strength at 24h using a Universal Machine Tinius Olsen. Internal morphology in bars fracture surface was evaluated by scanning electron microscopy using a FEI Quanta 200 3D microscope in low vacuum mode at pressure range between 5.5 and 6 Pa and acceleration voltage of 15kV.

RESULTS AND DISCUSSIONS

Figure 1 shows morphology and sizes distribution of NS. These particles are crystalline, with spherical morphology, and diameters varying between 2 to 10 nm. The calculated average size is 6 nm. As can be observed, these particles are well dispersed in aqueous media forming a hydrosol. Silanol (Si-OH) and Siloxane (Si-O-Si) bonds were identified in its chemical composition, besides surfactant agent and precursor residues that also were identified in FTIR spectrum (figure 2); Table 1 shows all identified bonds in NS hydrosol.

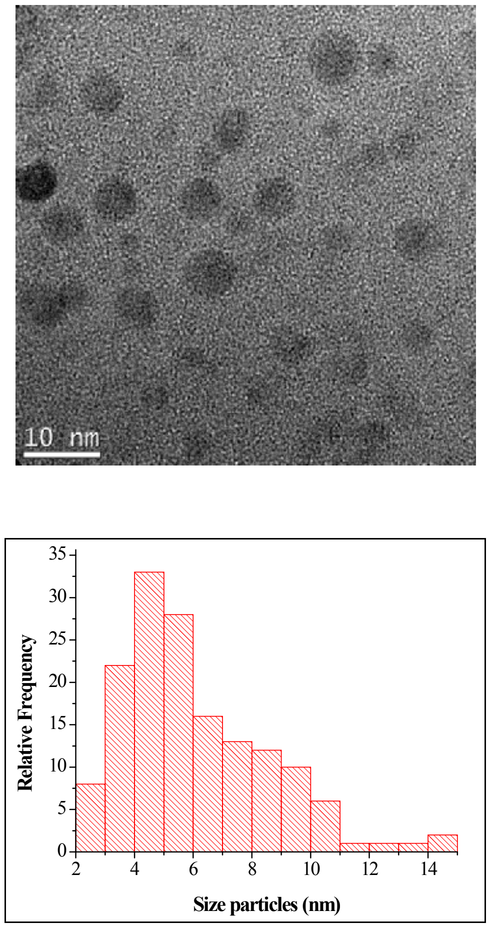

Fig. 1. Morphology and size distribution of NS.

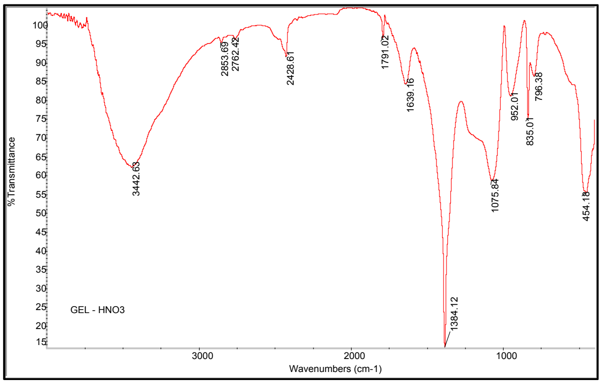

Fig. 2. FTIR spectra of NS hydrosol.

Table 1. Identified bonds in NS hydrosol

Wavelength (cm^{-1})	Group
450	Si-O-Si
815-840	Si-O-Si
800-1000	NO_3^-
900-1000	Si-OH
1000-1200	Si-O
1200-1400	NO_2^-, NO_3^-
1500-1700	H_2O
1700-2000	CH_2 (Triton X-100)
2350-2500	NO_3^-
~ 2750	CH_2 (Triton X-100)
~ 2850	CH_2 (Triton X-100)
3250-3500	OH/Si-OH/H_2O

Figure 3 shows the compressive strength values of the samples added with different contents of NS at 24h of aging.

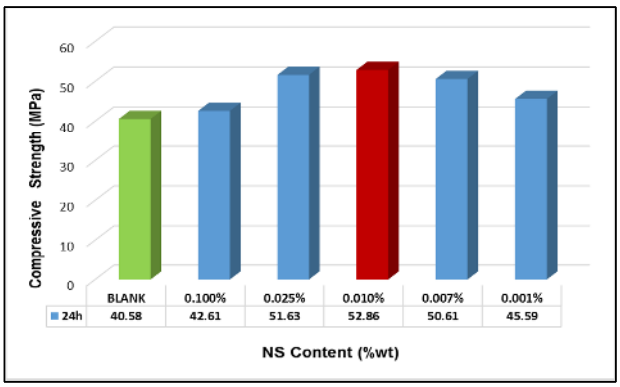

Fig. 3. Compressive strength of cement added with NS.

At low concentration of NS, (0.001-0.007% wt) an increase of compressive strength in comparison to the sample without NS, identified as blank, was observed. This increase is not significant since the quantity of NS is too low to generate large quantities of additional C-S-H gel. The highest compressive strength was detected in samples added with 0.01% wt of NS that show an increase of 30.3% related to the sample without NS (blank). In this case, NS remain disperse in aqueous solution, as is shown in figure 1, and due to their high superficial area, they enhance the production of C-S-H gel, based on the chemical reaction of NS and Portlandite [$Ca(OH)_2$] generated during cement hydration process. It is worth to mention that NS hydrosol also contributes to increase the solution reactivity allowing the use of very low quantities of NS.

At NS contents higher than 0.1% wt, the hydrosol tends to gelate (forming agglomerates) due to the low quantify of water added to the mixture according to standards ASTM-109M [6] and ASTM-348 [7].

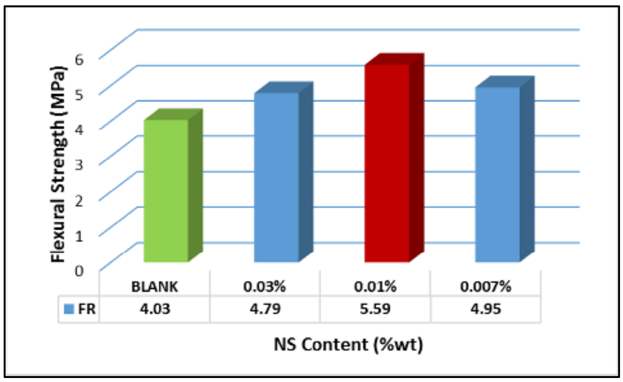

Fig. 4. Flexural strength of cement added with NS.

The same behavior is observed for the flexural strength tests, where the maximum value was obtained for the sample with NS content of 0.01% and shows 38.42% of resistance increase in comparison to the sample without NS (blank).

Figure 5a and 5b show the internal morphology of mixture of blank sample and cement added with NS

(0.01% wt) respectively. These micrographs were obtained in fracture surface of the flexural strength test bars.

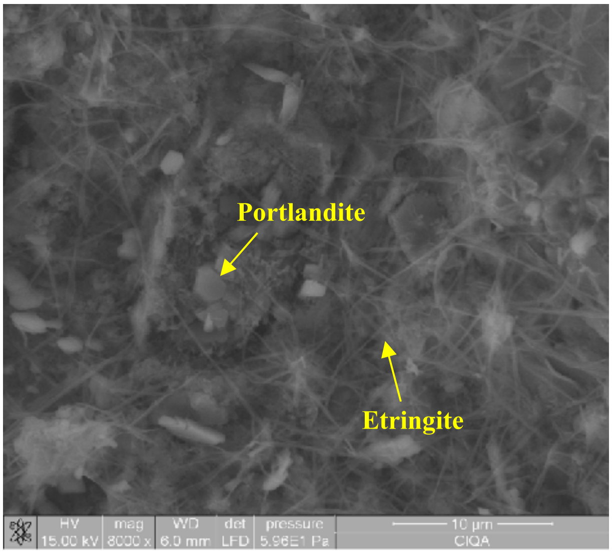

Fig. 5a. Microstructure of cement without NS

In the microstructure of blank sample (5a), hexagonal crystals, characteristic of Portlandite are observed. These crystals are prone to leaching and to react with sulfates forming calcium trisulfoaluminate known as Etringite, which is formed by needle like crystals that could form a net that contributes to the adherence of concrete in the first curing stages, but later stages, these crystals, can cause expansion, promoting the cracks formation inside the cement matrix.

A huge quantity of Etringite is observed, which indicates that most of the Portlandite crystals are transformed.

On the other hand, microstructure of cement added with 0.01% wt. of NS, shows a large quantitity of Portlandite crystals, and only a few Etringite needles are observed, which could be attributed to the fact that NS particles react with Portlandite forming additional C-S-H gel, but the NS concentration is not enough to react with all the Portlandite crystals.

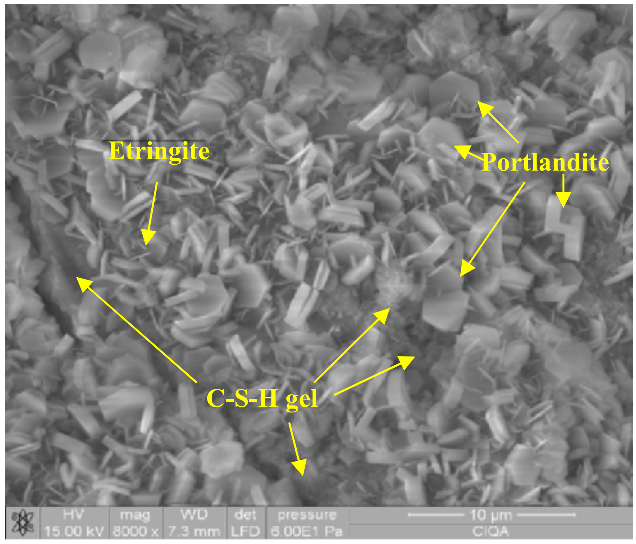

Fig. 5b. Microstructure of cement added with NS (0.01%wt).

Energy dispersive spectra of Portlandite and Etringite crystals are shown in figures 6a and 6b, respectively. Portlandite (Fig. 6a) shows mainly evidence of Calcium, Oxygen, and Carbon, besides Silicon, Sulfur, Magnesium and Aluminum. Etringite (Fig. 6b) shows mainly evidence of Calcium, Potassium, Sulfur and Oxygen, also shows evidence of Aluminum and Silicon, attributed to sulfate reaction.

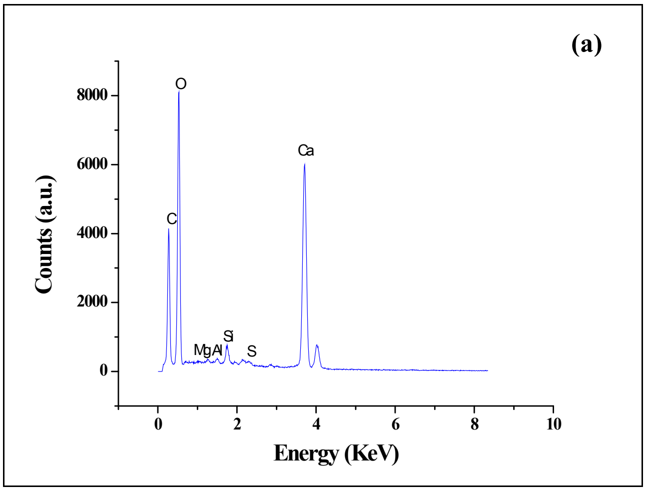

Fig. 6a. Portlandite EDS spectrum.

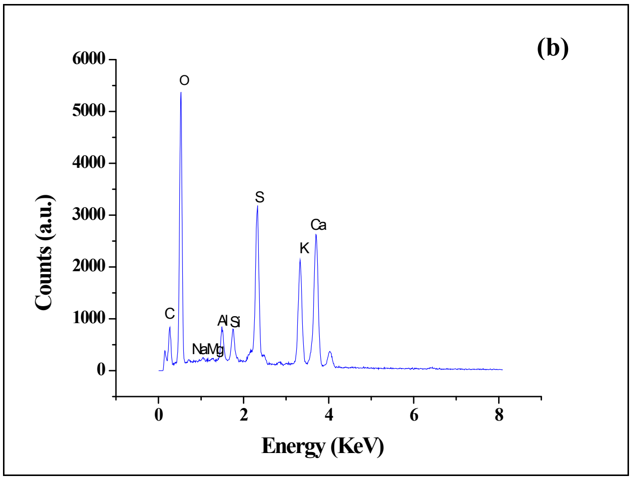

Fig. 6b. Etringite EDS spectrum.

CONCLUSIONS

A stable NS hydrosol was obtained by sol-gel method using a non-ionic surfactant. NS particle average size is 6 nm. Mechanical properties of cement Portland 30R are improved when it is mixed with small contents of NS dispersed in aqueous media due to their size, and well dispersion in aqueous media. An optimal NS content was established for the mixture with the best mechanical properties, which is attributed to the formation of additional C-S-H gel into the cement systems. At higher NS contents, the particles are not well dispersed in the matrix and form agglomerates of micrometric size that decrease the effect of NS. These agglomerates are formed due to the little amount of water used for cement slurries formulations according to ASTM C109M, ASTM-C348. At low contents of NS, the quantity of NS particles is too small to show a significant effect on mechanical properties.

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REFERENCES

[1] Maheswaran S., Bhuvaneshwari B., Palani G.S., Nagesh R.I., Kalaiselvam S. (2012) "An Overview on the Influence of Nano Silica in Concrete and a Research Initiative" *Research Journal of Recent Sciences* 2: 17-24.

[2] Perera, Y., (2010) "Preparation of nano-ceramics via aqueous sol-gel method modified with surfactants: an overview" *Materials Science Forum* 644: 79-84.

[3] Mondal P., Shah S.P., Marks L.D., Gaitero J.J. (2010) "Comparative study of the effects of microsilica and nanosilica in concrete" *Journal of transportation research board*: 6-9.

[4] Giraldo M.A., Tobón J.I., (2006) "Mineralogical evolution of Portland cement during hydration process" *Dyna* 148: 69-81.

[5] Schott J.A., Perera-Mercado Y.A., Corral V., García-Rodríguez S.P., Saucedo J.A. (2013). "Producción y evaluación de nanopartículas de sílice sobre las propiedades mecánicas del cemento Portland compuesto 30R" *Proceedings of International Multidisciplinary Joint Meeting of Nanoscience and Condensed Matter Physics 2013*. Morelia, México.

[6] ASTM-C109-11 Standard Test method for Compressive Strength of Hydraulic Cement Mortars.

[7] ASTM-C348-11 Standard Test Method for flexural strength of hydraulic-cement mortars.