

# Nanoparticles usage tendencies in cementing systems for hydrocarbon wells

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## NANOPARTICLES USAGE TENDENCIES IN CEMENTING SYSTEMS FOR HYDROCARBON WELLS

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### ABSTRACT

*In oil and gas wells construction, one of the most critical processes is oil well cementing, whose function is to provide a zonal isolation between the pipe and sedimentary formation. For these reasons, one of the needs in the oil industry, specifically in cementing wells area, is the use of materials with high performance, in order to enhance the useful well's life, and reduce costs associated with their repair or losses due to failures in the cementing.*

*Currently, the efforts in the area of high performance materials for oil wells cementing are focused on the development and use of Nanotechnology, science that study materials at nanoscale (10<sup>-9</sup> m) and offers means to obtain substantial changes in the chemical, physical and mechanical properties, due to the increase of their surface that allows them to have a high reactivity.*

*The cement is a complex mixture of inorganic chemical compounds, that contain mainly calcium silicates, aluminates (C3S, C2S, C3A), and gypsum. In the cementitious slurry preparation, the cement is put up in contact with water, producing the C-S-H gel as the main hydration product, with an amorphous initial structure that generate a mixture of solid final crystalline phases sometimes in the nanoscale sizes. This final structure is responsible for providing its mechanical properties. Therefore, their comprehension, modification and size control at nanoscale could enable the production of cementitious systems with improved properties.*

*The present work shows a resume of studies done in PDVSA Intevep on the synthesis and potential use of nanoparticles in diverse faces of oil well cementing and their use as nano-additives. Those papers were focused mainly on the preparation and laboratory-scale study of colloidal solutions of silica nanoparticles (nano-SiO<sub>2</sub>), Alumina (nano-Al<sub>2</sub>O<sub>3</sub>), iron oxides (nano-Fe<sub>2</sub>O<sub>3</sub>) and ternary systems of calcium oxide-silica and aluminium (CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>). Promising results were obtained on strength and cementing properties by adding nanosilica to the cement slurry formulations, and improvements on the mechanical properties, such as compressive strength at the order of 90% for 0.5% nanosilica concentrations based on weight of cement (BWOC).*

### WORK'S NOVELTY

*Nanoparticles have been widely used to significantly improve some materials properties, because they show unique physical and chemical characteristics, due to their nanometric sizes. Therefore, in PDVSA Intevep exist interest about the modification of certain properties of Portland cements used in oil and gas well operations, through the addition of nano-additives to the system, in order to solve specific problems in each stage of the cement life, from its placement, hydration, well's productive life, and even its abandonment, by means of manipulating cementing system properties, such as, cement phases hydration velocities, mechanical properties, permeability of the cement system already set, and others. In addition to the modifications and control of the cementitious slurry properties, our aim is to design an "intelligent cementing system", that would allow us to solve problems during different cementation stages and to obtain a cementing system able to stand the diverse pressures, temperatures and geomechanical conditions that are common in an oil well under construction.*

### MAIN CONTRIBUTIONS

*This study established the possibility to use nanosilica additive on cementitious slurries for oil and gas wells. Silica nanoparticles addition to oil wells cement improved its compressive strength, due to Calcium Hydroxide growth inhibition, resulting in the formation of an additional C-S-H gel structure, which improves the mechanical properties of cement. Furthermore, a better performance under compressive strength, at the order of 90% for 0.5% nanosilica concentrations BWOC in cement class B.*

**Keywords,** well cementing, nanoparticles, silica, CSH gel.

## Introducción

During oil well construction, the cementing process is vital, because a poor cementing operation brings drastic consequences, which include increased costs, risk of loss of the well, risks to the environment and security. The design of slurry cement should be prepared with a right design to resist the pressure, temperature and depth. Is why that, the oil industry there is a need to deepen in the development of high performance cementitious materials to enhance and improve the life of the well in order to reduce the costs associated with repairing or loss of fault-associated cementation.

Between the available alternatives for development and procurement of high efficiency cementitious materials is the nanotechnology application. The synthesis of nanoparticles has received considerable attention in view of the potential of obtaining new materials with mechanical, electrical, thermal, catalytic and optical properties with original and unique features. This has motivated several researchers to develop novel methods of physical and chemical synthesis. New methods of synthesis, or existing ones optimized, should enable the production of nanoparticles with a certain morphology, chemical homogeneity and surface characteristics to ensure the reproducibility of the method of synthesis (H. Nalwa, 2000).

About oil cement, to use nanoparticles involve to the synthesis of nanostructured compound, mainly to obtain nanophases of cement, which when are incorporated into cementitious slurries, could be to obtain a cement with physical, chemical and mechanical properties in order to improve efficient about itself for to resist critical conditions downhole.

In PDVSA Intevep, the researchers have prepared and studied on a laboratory scale, colloidal solutions of silica nanoparticles (nano-SiO<sub>2</sub>), alumina (nano-Al<sub>2</sub>O<sub>3</sub>) and ternary systems calcium oxide, silica and aluminum (CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>). The experiments were conducted through the incorporation of the nanosilica and ternary system in cement slurries. The results indicate the possibility to use nanosilica in cement systems, because the mechanical properties of the systems, such as compressive strength were about 90% for concentrations of 0.5% nanosilica BWOC, on the other hand, ternary system, introduced qualitative cementitious properties when reacting with water at atmospheric conditions. In the next section we show the results for each nanometer system.

### *Nanosilica system (nano-SiO<sub>2</sub>)*

In this study were mixed oil cement Class B with SiO<sub>2</sub> nanoparticles and were prepared solids samples in a cure chamber, them these samples were characterized some mechanical properties. The concentrations tested of SiO<sub>2</sub> nanoparticles were 0.10%, 0.30% and 0.50% based on the weight of cement and with variations in the aging time of nano system; finally it was explored with a formulation of slurry with commercial additives. To measure their mechanical properties were carried out measurements of compressive strength.

The results indicate that the cement mixture B, without any additional additive rather than the nanoparticles, have an increased compressive strength of the samples with the increase of concentrations Nano-SiO<sub>2</sub> in the systems. In this way, we obtain 25%, 56% and up to 70% profit on that property by the addition of 0.1%, 0.3% and up to 0.5% of Nano-SiO<sub>2</sub>, respectively, compared to

the samples without nanoparticles (see Figure 1). This is due to use of silica nanoparticles inhibits the growth of crystals such as calcium hydroxide  $[Ca(OH)_2]$  and Afm (monosulfate), which, by appearing as smaller crystals is not favorable to compressive strength of cement paste. On the other hand, the CSH phase production by the interaction between nano-SiO<sub>2</sub> and Ca(OH)<sub>2</sub> causes a direct increase in compressive strength in the cement system.

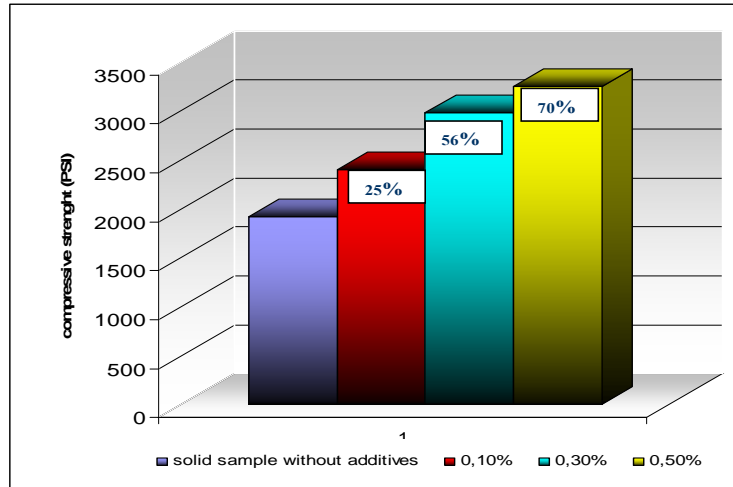


Figure 1. Compressive strength of cement mixture B with different concentrations of, Nano-SiO<sub>2</sub>

The Figure 2 shows for all concentrations of nano-SiO<sub>2</sub>, which increases as the aging time, there is an increased compressive strength of the last systems. This is because, in that as time goes on the reaction systems continue to produce chemical and nanostructural changes, for example, the polymerization stresses generated by the more stable nanoparticles due to the change of chemical bonds of type silanol (Si-OH) to siloxane (Si-O), which ones these result in a greater number of unsaturated bonds on the surfaces of these particles of two types:  $\equiv Si-O-$  and  $\equiv Si-$  and consequently coming back to the nano-SiO<sub>2</sub> more reactive when incorporated into cement pastes. Finally, we may observe how increases the compressive strength ranging from 20% to 91% values in the systems studied.

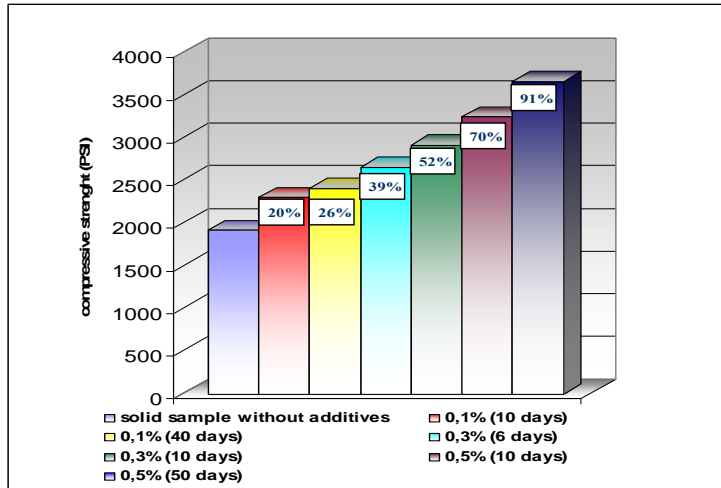


Figure 2. Compressive strength of cement mixture B with different concentrations of, Nano-SiO<sub>2</sub> and several aging time.

### *Nano-alumina systems (nano Al<sub>2</sub>O<sub>3</sub>)*

It was synthesised Al<sub>2</sub>O<sub>3</sub> nanoparticles by sol-gel method with nonionic surfactant. In the process we studied the effect of variables such as pH, temperature and solvent. The mineral Gibbsite was used as a precursor material. Subsequently, it was analyzed and characterized the resulting material through different conventional and unconventional methods. The HR-TEM and XRD results showed a crystallographic ordering of nanoparticles with sizes ranging from two to hundreds of nanometers, which varies in size depending on the calcination temperature.

In this study was not conducted tests of cement system functionalization with alumina nanoparticles, however, in the literature are reported several studies in which, use this type of nanoparticles in the Portland cement. In the cementitious matrix, the nanoalumina have similar behavior to nano SiO<sub>2</sub>, which reacts with portlandite (Ca(OH)<sub>2</sub>) for to produce hydrated calcium aluminosilicate (CAH) (pozzolanic reaction) and also acts to accelerate the hydration process. Al<sub>2</sub>O<sub>3</sub> nanoparticles act as nanoclusters, which is attached to larger particles and capilar area of the matrix, which causes a decrease in porosity and produces a direct increase in the mechanical properties of the systems, specifically in elastic modulus and compressive strength of the cementitious system (Figure 3) (Zhenhua Li et al, 2005).

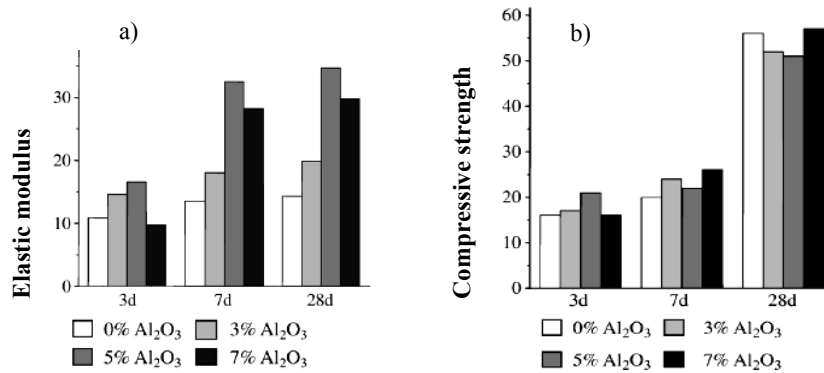


Figure 3. Mechanical properties development, in cement systems at 3, 7 y 28 days, with nanoalumina particles a) Elastic modulus and b). Compressive strength

### *Ternary systems (nano CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>)*

CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> nanoparticles were prepared from the sol-gel method modified with nonionic surfactant. During the process, were manipulated variables such as pH, temperature and solvent. The material was analyzed and characterized by various analytical techniques. The results obtained by HR-TEM and XRD showed the formation of nanoparticles with sizes ranging from two to hundreds of nanometers, depending on the calcination temperature.

Respect to the interaction of nanoparticles with cement systems, was determined their ability to react with water. For this, we mixed the nanoparticles produced at 1350 ° C with water at a ratio of 0.50 and 0.85. The Figure 4 shows the cement samples obtained.



Figure 4. Cement samples from cement systems produced at 1350 °C with different water ratio. (a) 0,50 ratio; (b) 0,85 ratio.

The results showed that both water/cement ratios, materials were obtained with one day of cured. However, this material was less fragile than one shown at 7 days of curing, in fact, the sample was fractured with less effort. In appearance, the samples obtained were equal across the entire surface, however, for 0.5 ratio (used in conventional cement) unhydrated granules were observed, which may be due to the requirement for more water for hydration of nanostructured materials by their high surface area. Similar results were obtained by S. Halim et al., (2007), who used water / cementitious nanoparticles of 0.2 and 1.25 with a curing time of 1 and 7 days.

The Figure 5 shows a micrograph obtained by scanning electron microscopy of a powder from samples hydrated and calcinated at 1350 ° C. Porous appearance was similar in all samples. In addition, the microstructure obtained shows that at one day of hydration did not form a compact material completely, which confirms the need for more cured time. Halim et al., (2007) also indicate that the porosity in nanostructured materials is related primarily to the amount of water used, if this is not enough the reaction will be limited in some areas of the cementitious matrix nanoparticles as discussed above. The detailed view of Figure 5 confirm the previous micrograph, where there is overgrowing in some areas of hydrated material.

Finally, in order to decrease the porosity and increase the strength of hydrated nanoparticles, it should increase the cured time for to obtain a better development of the hydraulic properties and could be used in the future as a possible addition both nanoparticles in Portland cement for oil wells.

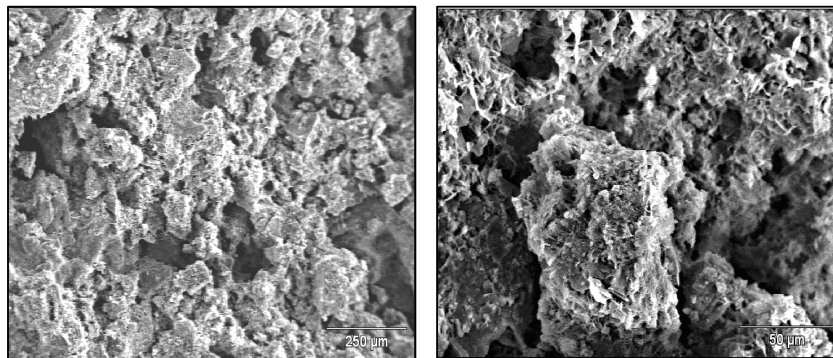


Figure 5: Micrograph obtained by scanning electron microscopy of a powder from samples hydrated and calcinated at 1350 ° C.: (a) General view; (b) Detailed photomicrograph.

## Conclusions

- The properties studies of cement-nanosilica give the possibility of using this type of nanoparticles in cements systems.
- Increasing the concentration of nano-SiO<sub>2</sub> in pure cement matrices B generates increased in compressive strength
- By increasing the aging time of nano-SiO<sub>2</sub> systems increases compressive strength, as result from the condensation and polymerization of the structure of silica.
- There is the possibility to study the inclusion of nanoparticles of alumina slurries for cementing oil wells construction because these can act as nanoclusters that are attached to larger particles of the matrix, which causes decrease in porosity and produces a direct increase in the mechanical properties of the systems, specifically in elastic modulus and compressive strength of cementitious system
- Respect to ternary systems, in order to decrease the porosity and increase the strength of hydrated nanoparticles, it should increase the cured time for to obtain a better development of the hydraulic properties and could be used in the future as a possible addition nanoparticles in Portland cement for oil wells.

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