Smart Cement Modified with Nano Fly Ash and Micro Fiber for Oil Well Applications.

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Abstract. Adequate slurry design is critical to the success of a cementing work. In this study, a ball mill procedure was used to prepare a nano powder from a fly ash material supplied by Al-kufa Cement Factory for re-inforcing the oil well cement through using it as a partial replacement of oil well cement class G by a weight percentage of (0.25%, 0.5%, 0.75% and 1%) and micro fiber polypropylene at percentage (0.25%, 0.5%, 0.75%, and 1%). The mix with a water to cement ratio was made at 0.44. Characterizations of the prepared samples were conducted by X-Ray Diffraction (XRD), Atomic Force Microscope (AFM), density and compressive strength. The results manifested that the structural properties were improved with the development of calcium silicate hydration (C-S-H) phase, the density as well as the enhancement in compressive strength. That makes it proper for the oil well applications.

1. Introduction

Nanotechnology is not a new science and it is not a new technology. It is rather an extension of the science and technologies that have already been in development for many years and it is the logical progression of the work that has been done to examine the nature of our world at an ever smaller scale. Nearly every aspect of the construction process will be touched by the foregoing innovations of nano scale technologies [1].

The nano scale size of particles can result in dramatically improved properties from conventional grain size materials of the same chemical composition [2].

Processing of the nano materials and their applications, normally if the particle sizes are in the ranges of (1-100) nm ranges, they are generally called nano-particles or materials [3].

Materials at Nano scale have a relatively larger surface area when compared to the same mass of material produced in a larger form that’s make it more chemically reactive (in some cases materials that are inert in their larger form are reactive when produced in their nanoscale form), and affect their strength or electrical properties [4].

The cement used in oil wells is a classify as class G cement, that variation of the Portland cement with low content of celite (C3A) and with bigger grains than the other common Portland cements [5]. Oil well cement (OWC) slurries is generally more complicated than that of conventional cement paste, In order to contend with bottom hole conditions (wide range of pressure and temperature), a number of additives are usually used in the OWC slurries, which exhibit different characteristics depending on the
Combination of admixture used incorporating various chemical and mineral admixtures used [5].

Cementing job is the process of placing cement slurry to the desired location in the annular between casings and wellbore with general function to bond the casing and formation, to prevent migration of formation fluids between zones and to control lost circulation. The slurry properties which are generally considered to be important include; density, fluidity, setting time or pumping time, strength, stable suspension of particles, free fluid or free water; ability to resist dehydration against permeability – fluid loss; permeability, shrinkage and durability. The cement must last a long time – longer than the well – and prevent fluids moving between the subsurface and surface [6].

Several studies were conducted for many years on the using of nano-powders and fiber in well industry and their effects on the properties, performance, and application of the cementious materials. In 2015 J. D. Mangadlao et al [7] made a review of summarized the importance and approaches of smart cement materials. For a variety of industries including the oil and gas production sector, the use of smart cements can lead to cost-effective solutions that may well result in on-time drilling operations and new monitoring protocols in asset integrity management. The review has emphasized the features and the stages of the cement materials and current efforts underway to fabricate smart cements for a variety of applications. The application of nanotechnology and stimuli-responsive systems will result in true advances in materials and technologies for the oil and gas production in upstream operations. Have study the use of a polycarboxylate superplasticizer to improve the dispersion of graphite oxides (GO) in cement. A 48% increase in tensile strength was observed for graphene-cement nanocomposites containing 1.5wt% GO and 0.5 wt% plasticizer. They have demonstrated that the GO nanoplatelets were well dispersed and no GO agglomerates were seen in the matrix. Babak et al., 2014 [8] studied the aforementioned advantages that include higher compressive and tensile strength; excellent durability and corrosion resistance make this new class of material highly attractive for applications in construction industry. Particularly, it is highly applicable for well cementing and construction on offshore and other structures in marine environments. Wu et al., year [9].

GO as an additive to concrete do not only enhance mechanical property but may also prevent Microbial Induced Corrosion (MIC) of concrete, which is a very common problem in oil wells. Graphene oxide has antibacterial property that can inhibit the growth of a wide range of bacteria such as Escherichia coli (E. coli) and Bacillus subtilis (B. subtilis) and Cupriavidus metallidurans (C. metallidurans) [10].

In 2017 by S.M. Ragehet al [11], prepared the cement prepared for testing at a temperature of less than 250°c. In this research, cement class G is used, in addition to accelerators and retardants, was used at certain percentages after completion. They measurement of thickening time, free water content, viscosity, rheological properties, fluid loss and various other properties and compressive strength after two day they note that the addition of the Accelerator. fcOur results do support my hypothesis. The test we did went on very smoothly only place where we struggled was in finding the best equipment to perform the experiment, since the rate of temperature has to be constant for the mixing. Thickening time and compressive strength correlations for Portland – class "G" cement slurries have been estimated. The test further went on ahead to come to conclusion that the additives effect the compressive strength and the thickening time of class G of cementing oil well. In 2015 C. Vipulanandan et al [12], study the objectives was to quantify the effect of different w/c ratio on the electrical resistivity and piezoresistive behavior of smart oil well cement. In this study, Class H cement with water-to-cement of 0.38, 0.44 and 0.54 was used. The samples were prepared according to the API standards (API 1997, 2002). To improve the sensing properties and piezoresistive behavior of the cement modified with 0.1% of conductive fillers (CF) by the weight of cement was mixed with all the samples. After mixing, cement slurries used for rheological, curing and piezoresistivity studies. Two conductive wires were placed in all of the molds to measure the changing in electrical resistivity. At least three specimens were used for each type of test for all the water-to-cement ratio mixes investigated in this study. Experimental and analytical modeling of the rheological and piezoresistivity behavior on smart cement with w/c ratio of 0.38, 0.44 and 0.54, show that The rheological test showed that class H oil well cement had shear-thinning
behavior and a hyperbolic model was proposed to predict shear stress–shear strain rate relationship. The hyperbolic rheological model predicted the test results very well compared to the Herschel Bulkley model. The yield stress and maximum shear stress limit reduced with increase in water-to-cement ratio while increasing the temperature increased these properties. The initial resistivity \( \rho_0 \) of the smart cement decreased from 1.03 Ω-m to 0.9 Ω-m, a 3% and 13% reduction with increasing the water-to-cement ratio from 0.38 to 0.44 and 0.54 respectively. Hence the electrical resistivity can be used for quality control. Water-to-cement ratio affected the curing characteristics \((\rho_{\text{min}} \text{ and } t_{\text{min}}) \) of the cement. The smart cement showed enhanced piezoresistive behavior compared to unmodified cement. With 0.1% conductive filler (CF) modification the piezoresistivity at peak stress was enhanced by over 700 times the unmodified cement. The piezo-resistivity enhancement was depended on the water-to-cement ratio and curing time. The new piezoresistive constitutive model predicted the compressive stress—changes in resistivity relationship very well. Additional of 0.1% CF also increased the 28 day compressive strength by over 10%. The resistivity index \((R124 \text{ h}) \) of the smart cement with lower w/c ratio was higher than that of the cement with higher w/c ratio. Linear correlations were determined between resistivity index and compressive strength of smart cement for different curing times.

There were two local researches on the effect of adding Nano material to the cement slab in terms of compressive resistance, thickening time, density where, In2017 H. A. Hadi et al.[13], study experimental investigation of nano alumina and nano silica on strength and consistency of oil well cement. In this study the cement powder used Glass G (HSR) cement according to API standards, was provided by Missan Oil Company and Nano Alumina and Nano Silica are used as additives to cement slurry at percentage (1%, 2%) of Nano silica by weight and (1% , 2% , 3%) of Nano Alumina by weight. They placed cement slurry to be tested in the prepared molds and placed the specimens in the curing bath at atmospheric pressure and heating to test temperature 38 °C for 8 hr and to the second test temperature 60 °C for 8 hr. After tested it they show Compressive strength of oil well cement at 38°C is increased when amount of NS&NAL is increased. The reason of this strength improvement is due to the small size of nano particles in pores between cement particles; therefore, it increased the efficiency of the packing. The second reason is due to the effect of (NS&NAL) on promoting the Pozzolanic interaction. That means it reacts chemically with Ca(OH)2 (formed from dehydration interaction) at ordinary temperature in the presence of water and produce compounds having cementitious properties. At 600°C compressive strength is decreased when the amount of NS exceeds 2% bwoc. This means that raising the quantity of NS is good in increasing compressive strength to a specific cutoff after which further increase in the NS quantity leads to a reducing in the compressive strength. The reason for that truth is the additional rate of NS could prompt agglomeration of its particles under the present dispersion circumstance. Nano materials (NS and NAL) accelerated the thickening time of cement slurry class G. and in 2014 by A. A. Abdulrahman et al.[14] was studied, Characterization of Nanosilica from Iraqi Rice Husk and its Application in oil well cement. The objectives of this research are Preparation of nanosilica from Iraqi rice husk by two chemical precipitation methods. And Studying the compressive strength of oil well cement class G by using different percentage of nano silica. Aim of this paper is Preparation of nano powder from fly ash material resulted from kufa cement factory.
for supporting OWC using produced nano powder as a partial replacement OWC and Characterization the prepared sample using Scanning Electron Microscope (SEM) observation, X-Ray Diffractometer (XRD) and Atomic Force Microscope (AFM). Studying the compressive strength test of oil well cement class G slurry at different percentage by Nano fly ash and Polypropylene fiber in order to improve cement properties such as cement improvement and mechanical properties improvement to make it suitable for well properties.

2. Experiment

The experimental step of this section of study was designed to investigate the effect of adding nanoparticles on the mechanical, physical, structural properties of cement glass cement glass mixtures were prepared using two different groups of nano materials and one micro fiber which are (Nano flyash, polypropylene fiber) in five concentrations (0.25%, 0.5%, 0.75%, 1%) per weight for nano materials but by volume for micro fiber. In order to achieve these steps, number of sample cement are designed For oil well cement class G must apply 792gm weight of cement and 349gm water, according to API (American Petroleum Institute, 1997) in nine classes (from A to J) the percentage of nano materials and micro fiber was (0.25%, 0.5%, 0.75%, 1%) by weight of the cement material for nano materials but by volume for micro fiber. Cement glass G with nano materials (flyash) and micro rod (polypropylene fiber) were compared with reference mixture to evaluate the effect of the dosage of nano materials and micro fiber.

Chemical composition test for cement and fly ash was performed in the Iraqi geological survey department ministry of Industry Baghdad Iraq. Density test was done according to (ASTM C-373) standard[15], the true density (p_t) is prepared by setting model in the water (Archimedes rule) via following connection [16-17]:

\[ p_t = \frac{W_d}{W_s - W_n} \times D \]  \hspace{1cm} (1)

where \( p_t \) is true density (gm/cm^3), \( D \) is density of distilled water (1gm/cm^3), \( W_d \) is dry weight of sample (gm), \( W_s \) is weight of sample after saturation in water (gm), and \( W_n \) of sample when submerged in water (gm). Atomic force Microscopy (AFM) was taken with digital instruments; typical data have been taken from height images including root mean square (RMS) and roughness. made in USA model AA300220V. Compressive strength test for cubes samples was determined by using a universal measurement machine (EVERY DENISON) of 2000KN capacity. The average result of three specimens was reported for each sample. The following relationship was used:

\[ \sigma = \frac{P}{A} \]  \hspace{1cm} (2)

Where \( P \) is ultimate compressive load, \( (N) \) is sample area, \( (\text{mm}^2) \) and \( \sigma \) is compressive strength (MPA).

The X-ray diffraction was taken by diffractometer with radiation CuKa (\( \lambda = 1.54060 \) A) this inspection was carried out in Nano technology and Advance Material Research center at the university of technology. Particle size test for powder fly ash was performed in nanotechnology and advanced research center (model: Brookhaven Nano Brook 90 plus USA), it was 100nm.

| TABLE 1. Chemical composition of raw materials (Cement Glass G) |
|-----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Material       | SiO_2          | Fe_2O_3        | Al_2O_3        | TiO_2          | CaO            | MgO            | SO_3           | LOI            |
| weight%        | 30.38          | 2.61           | 5.95           | 0.33           | 42.64          | 3.80           | 1.840          | 7.97           |

| TABLE 2. Chemical composition of raw materials (Fly Ash) |

The following relationship was used:
3. Results and Discussion

Figure 1 shows the Density of the prepared samples. Nano powder plays a filler role in order to enhance the density of the samples, which can decrease the porosity of mixture; on the one hand powder can accelerate cement hydration by virtue of their high free energy. Also by adding the PF improve the density of the samples as it can shows in the fig.1.

![Graph showing density of prepared samples](image)

**Figure**: The Density of the prepared samples.

Compressive Strength Result

Figure 2 shows the compressive strength: The compressive strength and capability of mortar with "nano
fly ash” were the outcomes linked with G class Cement Mortar GC, mortar and "nano fly ash" were produced to be long-lasting more than Normal Cement Mortar "NCM" and the measuring size will be growing by the strong point of mortar with "nano - fly ash" with different to GC that founded to be in the diversity between 17 % to 50 % for a range of symbols of mortar, the capability of mortar with "nano - fly ash" has been created to be very much more than GC, It is recognized that the porosity and pore volume distributing are critical combination of "microstructure hydrated cement dentifrice", the effect strength orderly to gain high strength reducing the permeability and a toughing form of mortar is urgent to reduce the porosity of cement dentifrice it is very familiar that the mixture of "pozzolanic (CSH)" materials of cement smooth the porosity and pore size distributing of the dentifrice. Fly ash is identified to be a high-quality "pozzolanic" material to be used with mortar, many researchers investigator have documented these effects on the physical characteristics and pore structure, researching proof the effect of "fly ash" purity at the compressive strength pore size distributing and porosity of reinforcement cement dentifrice. category C fly ash "high - calcium" with nano particle dimension about (100 nm) also it has been using with partially replaced with Portland cement on (0 , 0 . 25 , 0 . 5 , 0 . 75 , and 1 wt% ) by loading the water to cement proportion (w / c) of (0.44) was intended for all the blended cement dentifrice mixture, the totality porosity and capillary pores were decreasing whilst the gel pore has better than previous situation because adding "nano fly ash" at all substitute levels [18 , 19 , 20]. The examination sequel submit that the blended cement dentifrice at high (1 %),"nano fly ash" has been shaped a dentifrice with better compressive strength than (0.25) nano fly ash, the porosity and pore size of blended cement dentifrice were severely affect by the adding more "nano fly ash", the substitute of Portland cement by "nano fly ash" has bigger than previous to the porosity other than reduce the average of pore size of dentifrice the calculated gel porosity (5.7-10 nanometer ) had improve by increasing the "fly ash content".

Figure 2: The compressive strength of the prepared samples.
Atomic Force Microscopy Result
AFM is a powerful technique to investigate the surface morphology at nano to microscale. The surface of mortar is shown in fig. (3) 3D of the surface, the roughness of mortar surface without the addition of
fly ash was 18.79 nm, while in the presence of 0.25 Wt% partial replacement of cement by nano fly ash was 15.38 nm and in percentage of 1% fly ash surface was 20.17 nm. The difference depends on the rate of replacement of cement with nano powder. From AFM test, also it can be seen that mortar without adding Average Diameter 103.01 nm in 0.25 FA was. Diameter 184.82 nm and in 1%FA was Avg. Diameter: 158.30. nm.

Table 3. shows the AFM result of Glass G only and with additives.

| Percentage% | Roughness nm | Diameter nm |
|-------------|--------------|-------------|
| Zero sample | 18.79        | 103.01      |
| 0.25% PF    | 37.21        | 232.64      |
| 1% PF       | 73.76        | 124.39      |
| 0.25% FA    | 15.38        | 184.82      |
| 1% FA       | 20.17        | 158.30      |
| 0.25%FA + PF| 49.29        | 206.84      |
| 1% FA + PF  | 29.27        | 133.20      |

**X-XRay Diffraction Result**

Figure 4 shows the XRD pattern of the cement mortar without nano powders, cement mortar (after curing time) of the (reference and mixed specimens), the components of phases are shown in the Figs from 4-b to 4-c. Were: Portlandite: Ca(OH)2, hexagonal crystallized, JCPDS (04-0733)(CH), Tobermorite:Ca5Si6(OH,F)18.5H2O,orthorhombic crystallized, JCPDS (45-1480) (Tob), Ettringite:Ca6Al2(SO4)3(OH)12.26H2O,hexagonal crystallized, JCPDS (41-1451) (CASH).
Furthermore, the phases shown were: - Calcium Silicate Hydrate: CaO·SiO₂·H₂O, poor crystallized, JCPDS (34-0002) (CSH), Wollastonite: CaSiO₃, monoclinic crystallized, JCPDS (43-1460) (CS). It was observed that the ettringite and portlandite are involved in all stages of the hydration. In addition, the changes that happened in mineralogical components during the hydration processes were observed, where hydro-silicates and hydro-aluminates were present (portlandite, tobermorite and ettringite), the highest peaks correspond to portlandite (CH) and calcium silicate hydrated (C-S-H) gells [21], XRD characterization were done in order to investigate the activity of the incorporated nano powders with cement mortar specimens after hydration, from the XRD patterns it is clear that the (CH) peaks are nearly decreased with mixing by (fly ash) nano powders, it is therefore inferred from the figures below that nanopowders can react with the produced CH through the hydration. Hence, the reactivity of nanopowders is significantly high and has developed the microstructure of cementitious materials, thereby it has improved the mechanical properties of cementitious materials, and CH compound has a sharp peak in the cement mortar acting as the pure hydration product, which is released from the hydration of cement. Obviously, the peak/intensity of CH is reduced due to the nanopowders as a cement replacement as shown in the Figs. from (4-b) to (4-c), which show the consumption of CH via the pozzolanic reaction [22].

![XRD pattern of the G cement mortar](image)

**FIGURE 4.** XRD pattern of the G cement mortar; a: without nanopowders (b): 0.75% FA, (c): 1% PF (d):1%FA+PF

4. CONCLUSION
When nano powder as partial replacement of Portland cement in mortar result increase in the density and a rise in the compressive resistance, increased pozzolan interaction this leads, as well as roughness of the surface decrease with increase fly ash. The Polymer fiber also act as binder material, mainly used to enhance the shrinkage cracking resistance and toughness Polypropylene fibers are commercially utilized at relatively low volume fractions to control plastic shrinkage cracking of concrete. Polypropylene fibers are not expected to increase the strength of concrete, but to improve its ductility and toughness, and impact.
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