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Studying The Effect of Nano-Metakaolin Admixture Material On Mechanical Properties of Oil Well Cement (OWC)

Abstract- *This work aimed to study the effects of incorporate Nano-metakaolin (NMK) as pozzolonic material on some mechanical properties (compressive strength) of Oil Well Cement (OWC). Nano-metakaolin (NMK) was prepared from Kaolin rock brought by thermal activation of kaolin clay at different temperatures (700–800 °C) for 2 h then crushing and ball milled for (40-60) hours. The cement used in this study comprise of Oil Well Cement class G and NMK were incorporate as a partial replacement additive by NMK of (3%, 6% & 10%) by weight of cement with two different average particle sizes (75nm,100nm) and a w/c of 0.44. Several techniques were used to prepare and characterize NMK Particle Size Analyzers (PSA), X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and the Brunauer-Emmett-Teller (BET). The results showed and approved that the NMK was not only work as filler, but also as an activator to consolidate hydration process, through NMK particles react and consumes calcium hydroxide CH crystals to produce more C–S–H, fills pores to increase the strengths, decrease the size of the crystals at the interface zone and transmutes the calcium hydroxide feeble crystals to the C–S–H crystals, and upgrade the interface zone and cement paste domain.*

Keywords- *Nano-metakaolin, Oil Well Cement (OWC), Ball milling, Kaolin rock*

How to cite this article: A.D. salman, "Studying The Effect of Nano-Metakaolin Admixture Material On Mechanical Properties of Oil Well Cement (OWC)," *Engineering and Technology Journal*, Vol. 35, Part A. No. 9, pp. 909-913, 2017.

1. Introduction

In neoteric years, the employ of Nanoparticles as received special alertness in many frameworks of applications to innovate materials with new functionalities. When very fine particles (nanoparticles) are integrated in cement paste, mortar or concrete, materials with different features from classical materials were obtained. Oil-well cementing can doubtless be known as one of the most ticklish operations in petroleum and gas industry amongst all operations performed throughout oil or gas well drilling. Portland cement (PC) has been consumed as well cement for numerous years. However, Portland cement is not sufficient for some ticklish state of affairs, particularly in profound oil wells, geothermal wells, and corrosion environments wells. In elevated temperature and acidic milieu, the Portland well cement could lose strength, increased porosity and decreased durability in a shortened duration of time [1–6]. In the harsh environment lead to piecemeal deterioration of interconnection between admixture and cement paste matrix [7]. The output of an oil well was quite influenced by the cementing quality, and therefore well cementing is devoted to restrict movement of fluids between formations at different levels, shore vertical and radial loads utilized to casing, which is laid in the drilled borehole, and protect the casing from corrosion and sealing of abnormal pressure formations **[8-**10]. According to the American Petroleum Institute, specification for materials and testing for well cements (API Specification 10A, 2002) nine special classes of cements were established (Class A–Class J) [11]. In addition, OWCs are assorted into three grades based upon their C3A contents [12]. A vast assortment of cement admixtures is currently obtainable to improve oil well cement properties, to realize successful placement and rapid compressive strength improvement for suitable zonal isolation during the lifetime of the well [13-15]. Metakaolin vary from the conventional used different admixtures, such as (CNT), fly ash (FA), and silica fume (SF), that it is not a by-product. It is prepared by calcining kaolin under controlled conditions, one of the most abundant natural clay minerals, to temperatures of 700-900°C [16-17]. The resulting anhydrous amorphous aluminosilicate ($Al_2Si_2O_7$) also represented as AS_2 behaves as a highly reactive pozzolonic material react with $Ca(OH)_2$ to produce more (C-S-H). Newly, Nano technology has attracted considerable scientific interest because of the new possibility uses of particles in Nano meter (10^{-9} m) scale [18-19]. Subsequently, through the present study, the impact of NMK on the compressive strength of

https://doi.org/10.30684/etj.35.9A.7
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Oil Well Cement has been studied. To preparation OWC, efficacious and suitable for deep well we examined different dosage and particle size of NMK.

Abbreviations and nomenclature

NMK: Nano-Metakaolin
OWC: Oil Well Cement
NM3(75): Nano-Metakaolin according to the particle size analyzer for this group the average particle size is 75nm.and adding percent 3%
CM: Control mixture
(w/c): water-to-cementitious materials ratio

2. Experimental Work

I. Materials

Oil well cement (OWC) used in this investigation is Class G according to American Petroleum Institute (API) with a specific gravity of 3.15 g/cm^3.The chemical composition and physical properties of oil well cement class G(API-10A) are offered in Table 1. This cement was used in making ready all specimens. NMK was prepared by crushing and ball milling of Kaolin rock brought from (Dwekhla in Western Sahara, Al Anbar province). Chemical composition and physical properties according to X-ray fluorescence and Brunauer-Emmett-Teller (BET) of prepared NMK are shown in Table 2. Nano-metakaolin (NMK) ($Al_2Si_2O_7$) was prepared from Kaolin rock brought from (Dwekhla in Western Sahara/ Al Anbar province) by thermal activation of kaolin clay at different temperatures (700–800 ^oC) for 2 h then crushing and ball milled for (40-60) hours to reduce particle size NMK to Nano-scale as shown in Figure 1 describing practical steps of preparation. The specifications of equipment used during this work have been given in Table 3.

Table 1: Chemical and mineral compositions of oil well cement class G(API-10A)

Oxides	Wt%
CaO	64.21
SiO_2	19.40
Fe_2O_3	5.50
Al_2O_3	4.50
SO_3	2.80
MgO	2.00
Na_2O	0.10
K_2O	0.59
Loss on ignition	0.50
Density (g/cm^3)	3.15

Table 2: Chemical composition and physical properties according to X-ray fluorescence and Brunauer-Emmett-Teller (BET) of prepared NMK

Oxides	Wt%
CaO	0.17
SiO_2	55.07
Fe_2O_3	0.76
Al_2O_3	42.13
SO_3	0.15
MgO	0.05
Na_2O	0.05
K_2O	0.56
Loss on ignition 1.2	1.2
Particle size (nm)	**Specific surface area (g/m2)**
75	350
100	290

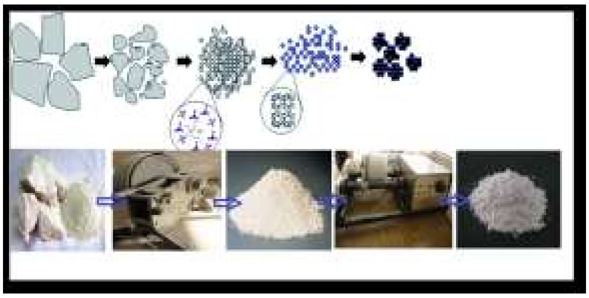


Figure 1: Practical steps of preparation process of Nano-metakaolin (NMK)

Table 3: Specifications of equipment's used

Equipment	Specification
Scanning electron microscope (SEM)	Type TESCAN
Atomic Force Microscope (AFM)	Angstrom, Scanning Probe Microscope, Advanced Inc., AA 3000A, USA
Particle Size Analyzers (PSA)	Malvern Mastersizer 2000
Ultrasonic	Soniprep 150 (120W, 60KHz)
Compression testing machine	ELE-ACCU-TEK 250.
Brunauer, Emmett and Teller (BET) method by surface area analyzer	Q Surf 1600, USA
X-ray diffraction XRD-6000	Shimadzu scan range is (10.0–60.0) deg.
X-ray fluorescence spectrometry	Shimadzu 1800
Electrical furnace	(100–1000) ^oC
Ball mill machine	300 rpm

II. Methods

A. Preparation and casting samples

Cement paste was prepared according to (API Specification 10A, 2002). A certain dosage of additives of NMK substitute by cement weight. Table 4 shows specifications and mixing attributions of cement samples. Initially, the weighed quantity of OWC It has been placed in a tureen. Thence, the weighed NMK admixture was added into the mixing distilled water. the mixing distilled water was decanting into the blender, then the weighed NMK admixture was added into the mixing water, then mix and dispersed nanoparticles by ultrasonic for 25sec.collecting and retrieve cement paste sticking accumulated to the wall of the mixing container by spatula to ensure homogeneity. At last, mixing take back for another 30sec at high speed. Thereafter, cement slurry was cast into 5cm cubes and then cured at 70°C with 100% relative humidity for 7 ,14 and 28 days to test compressive strength. In this study, three samples were tested for each mix. The average value was served as the final data.

B. Compressive strength test

The fresh cement slurry was put into a 500 ml glass-measuring cylinder cured in water bath at 70°C and allowed to stand for 2 hours to read free liquid volume directly. In addition, the fluid loss was tested by OWC-9510 high-temperature and high-pressure filter press at 70°C with 6.9 MPa. Compressive strength of the cement was tested by electronic-hydraulic pressure testing machine at a rate of 400 N/s(YA-300).

3. Result and Discussion

I. Characterization of Nano-Metakaolin

The Nano-Metakaolin obtained from ball milling process were verified by particle size analyzer. According to particle size analyzer, Metakaolin has successfully been reduced to particle size of 75 nm sized milling within (40) hours. According Atomic Force Microscope (AFM) Figure 2(A, B) shows the distribution of particle size for two different groups and at different milling time during the milling process. SEM image shown in Figure ٣ demonstrate ball-milled Nano-Metakaolin after 40 h of milling and Illustrates different textures of the (NMK) particles encompass spherical particles and unequal shape particles as well as agglomerates are due to constricting action of the ball-milling process. XRD pattern shown in Figure 4 shows that, the presence of mainly alumina and silica in the NMK prepared and confirmed polycrystalline structure.

Table 4: Mixing proportion of cement samples

Mixes	Mix proportion (Wt.%)		(w/c)
	OWC	NK	
NM0	100	0	0.44
NM3	97	3	0.44
NM6	94	6	0.44
NM10	90	10	0.44

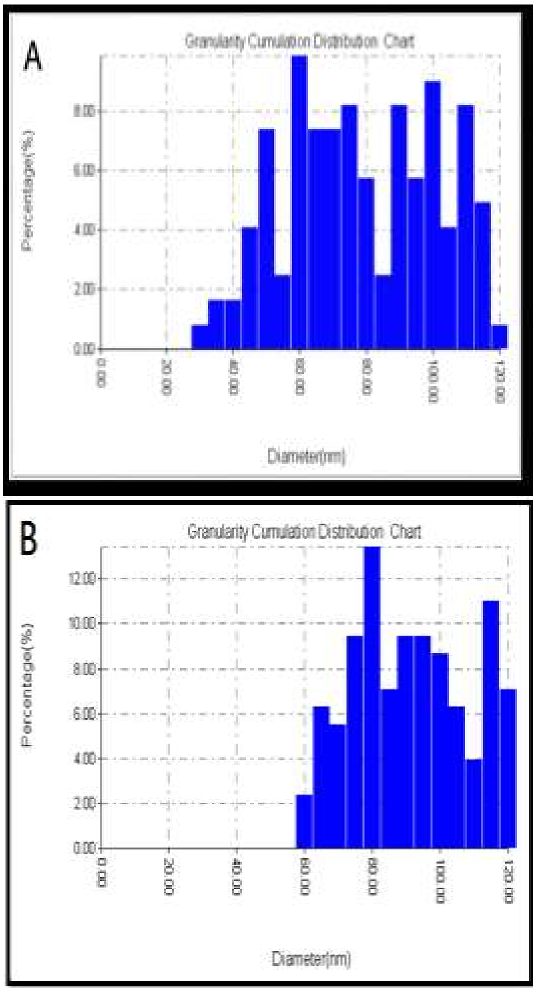


Figure 2: AFM of prepared (NM): A (100nm) and B (75nm)

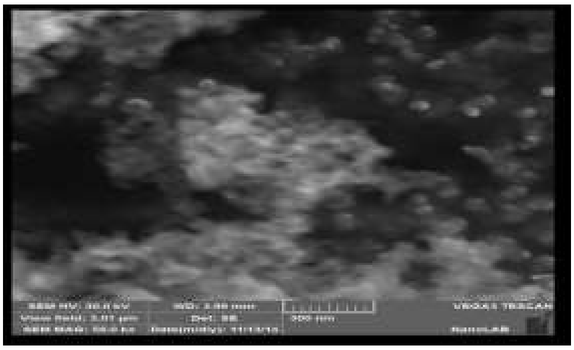


Figure 3: SEM image of the ball-milled Nano-Metakaolin

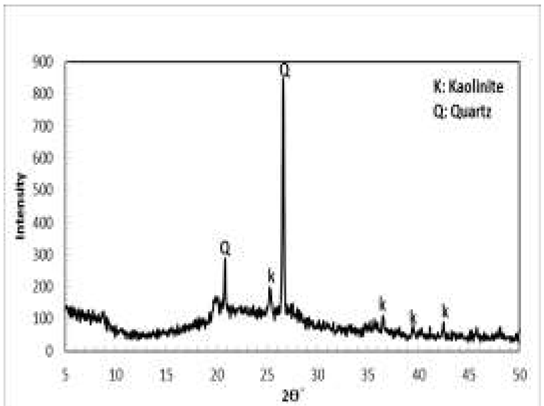


Figure 4: X-ray diffraction of Metakaolin 750℃

II. Compressive strength

A. Effect of (NMK) dosage on compressive strength development of OWC.

The compressive strength of hardened pastes made of Oil Well Cement (OWC) control mixture (without additives) and OWC with different dosage of NMK for all test ages (7, 14, and 28 days) are offered in Figure 5. For all ages of pastes, the diversity style of compressive strength of cement pastes with NMK was around congruous at the same temperature. At 70 ^{o}C, the NM6(75) specimen had a great strength at all ages than CM and cement pastes with NMK replacement, it is evident that the strength increased with an augmentation of NMK dosage to optimum concentration as shown in Figure 6. (a-b) This clarify that numerous the concentration of NMK is useful in improving strength to a certain limit after which any excess in the NMK dosage leads to a diminution in the compressive strength. The premature strength impact of NMK is inasmuch its effectiveness on accelerating the pozzolanic reaction and transform of C3S, C2S and $Ca(OH)_2$ into the C–S–H gel which is the causative for giving the matrix of OWC its strength. Huge early strength is also due to the high packing efficiency of NMK. Table 5 demonstrate the compressive strength results at 7, 14 and 28-days.

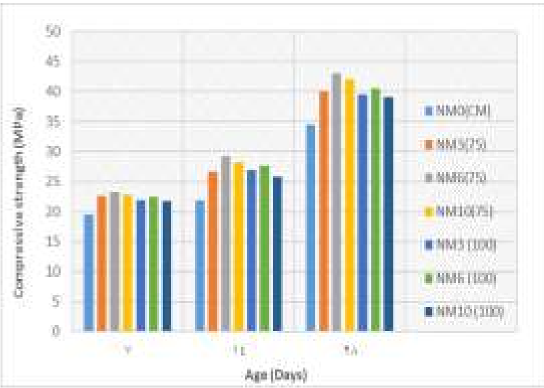
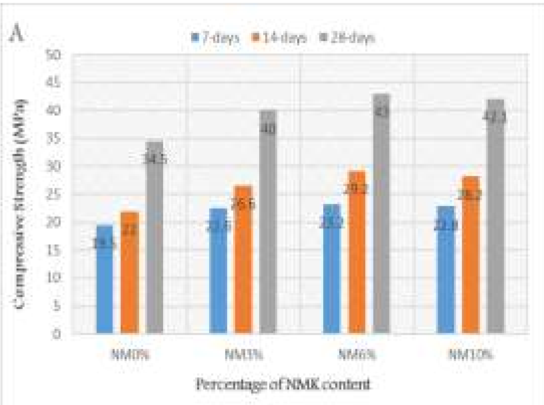


Figure 5: Effect of curing age on compressive strength of mixtuers



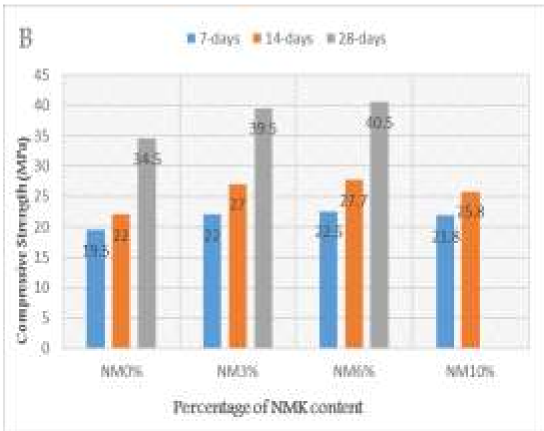


Figure 6: Effect of (NM) percentage on compressive strength of OWC for A (75nm) and B (100nm) NM.

Table 5: Compressive strength results at 7, 14 and 28-days

Mixture I.D.	Compressive strength (MPa)		
	7-days	**14-days**	**28-days**
CM	19.5	22.0	34.5
NM3 (75)	22.6	26.6	40
NM6 (75)	23.2	29.2	43
NM10 (75)	22.8	28.2	42.1
NM3 (100)	22.0	27.0	39.5
NM6 (100)	22.5	27.7	40.5
NM10 (100)	21.8	25.8	39

B. Effect of particle size of (NMK) on compressive strength development of OWC

The variation in the results seems to be a function of the particle size. For instance, the compressive strength of mixture NM6(75) nm had 43 MPa at 28 days slumped to 40.5 Mpa for mixture of NM6(100) nm. An impartial exegesis for this tendency is that as the particle size of NMK that enhance the packing adequacy decreases lead up to a decline in the compressive strength. This impact of NMK particle size on compressive strength can also be due to the huge surface area that is obtainable for pozzolanic reaction. It can be spotted from the outcomes that the surface area dropped with the altitude in the particle size as in other samples with NMK and as in the control mixtures (CM) which fructify less compressive strength at the same age. These outcomes are in good conformity with the measurement's obtained by [20].

4. Conclusions

According to the test outcomes, the following inferences can be drawn.

- Nano-Metakaolin (NM) was successfully obtained by Ball milling method for (30–60) hours with average particle size of 75 nm.
- The characterization of (NM) shows spherical particles having irregular shapes as well as agglomerates fuse together.

- Incorporating Nano-Metakaolin into Oil Well Cement mixtures enhances their mechanical properties, by yielding higher compressive than control mixture, and exhibit relatively high early strengths.
- Within the particle size and dosage range examined at all curing ages, the strength generally increases with the addition of NM, the optimum percentage of NM is (6%) with 75nm particle size gives the highest the strength of OWC mixtures.
- The results approved that the NMK was not only work as filler, but also as an activator to support hydration process, by consuming calcium hydroxide ($CaOH_2$) crystals to produce more C–S–H, and filling the pores to increase the strengths.

Acknowledgement

The author would like to thank everyone who has helped to complete this work, especially, Head of the Department of Chemical Engineering Dr. Mohammad A. Taher from Basrah University for Oil and Gas, Basrah -Iraq, for his contribution to testing and measurements.

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Previous publications

- Characterization of Nano-Silica Prepared from Local Silica Sand and Its Application in Cement Mortar Using Optimization Technique.
- Optimization Process for Using Prepared Nano Silica in Concrete.
- Comparative Study of the Effect Incorporating (amorphous-crystalline) SIO_2 Nanoparticles on Some Properties of Poly (methyl methacrylate) Denture Base Material.