Improvement of mechanical properties of Oil well cement by incorporate Nano-CaCO₃ prepared from eggshell waste

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Abstract

The objectives of this work were to prepare, characterize the CaCO₃ nanoparticles as admixture derived from eggshell waste to improve the mechanical properties and performance of oil well cement (OWC) and to evaluate the interactions regarding the cement-admixture compatibility. The results suggest to use the combination of ultrafine grinding (ball milling) and heating treatment. The evaluation of the effectiveness of the addition of eggshell nanoparticles (ESNP) on the mechanical properties (compressive strength) of OWC was also an important objective. The high purity of eggshell powder was milled for 5–30 h to prepare ESNP with an average particle size of 40 nm after 25 h. The physico-chemical properties of the ESNP were characterized by different techniques including particle size analyzer (PSA), X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy (SEM) and the Brunauer-Emmett-Teller (BET) methods. The ESNP was added in three different percentages to the OWC (2%, 6% and 10% as partial replacement of cement) and a w/c of 0.44. It was also revealed that the best percentage of ESNP addition not only resulted in much denser microstructure in OWC but also changed the formation of hydration products through presence of CaCO₃ nanoparticles, which increased the rate of reaction of tricalcium aluminate (C₃A) to form a carboaluminate complex. In this way the rate of hydration increased, the total hydration products increased and consequently the strength as well. Hence the addition of ESNP contributed to the improvement of early-age compressive strength, microstructure and durability properties of cement. According to the results, it was found that the optimal addition of ESNP to OWC is 6%.

Keywords: Eggshell nanoparticles, Oil well cement, Ball milling, Mechanical properties,
1. Introduction:

The eggshell (ES) is one of the most common biomaterials in nature. It is a very interesting material for potential waste treatment, because it is a by-product in food industry and after the production of eggs it is considered waste [1]. Chicken eggshell (ES) is an agricultural byproduct that has been listed worldwide as one of the environmental issues. The chicken eggshell wastes were applied as raw materials for the preparation of nano-calcite (CaCO₃) [2]. In recent years, limited studies have been conducted on the additions of nano-CaCO₃ as partial replacement of cement in concrete on the hydration and compressive strength modifying. Currently, the commercial additives were imported and the price is kept increasing year by year [3]. Therefore, the researchers were continuously looking for potential additives such as nanoparticle to improve the cement properties. Although the use of CaCO₃ was first considered as filler to partially replace the cement, studies have shown some advantages of using CaCO₃ in terms of strength gain, reaction rate accelerating effect and economic benefits as compared to cement and other supplementary cementitious materials [4,5]. Chemically, the presence of CaCO₃ nanoparticles increase the rate of reaction of tricalcium aluminate (C3A) to form carboaluminate complex thereby increase the total hydration products, delay the formation of micro-cracks, the total hydration products and consequently the strength [6]. In addition, it also reacts with tricalcium silicate (C3S) and accelerates setting and early strength development as shown in Fig.1 [7]. Physically, CaCO₃ nanoparticles filling the voids and pores in cement with the small size nanoparticles thus enhancing the strength and minimizing the porosity of the cement. In terms of durability properties, it was revealed that replacement of cement with limestone powder (CaCO₃) had significant effect on the resistance of sulphate attack and water absorption which is related to the filler effect, heterogeneous nucleation and the dilution effect of limestone powder (Ramezanianpour 2010) [8,9]. Elsewhere, Sato and Beaudoin (2011) carried out an investigation on the incorporation of micro- and nano-CaCO₃ with high volume of supplementary cementitious materials. In that experiment, cement was replaced with 50% fly ash and 50% slag and was incorporated with10 and 20% of micro- and nano-CaCO₃ by weight of the binders [10]. It was found that the replacement of cement with nano-CaCO₃ accelerated the early hydration of cement and enhanced the early development of modulus of elasticity as the amount of nano-CaCO₃ was increased. The presence of nano-CaCO₃ particles has been suggested to have a significant effect on the hydration kinetics of C3A and C3S which may cause acceleration of setting and early strength development [11]. Another study, Sato and Diallo (2010) reported the seeding effect of nano-CaCO₃ where the rapid growth of CSH was obtained on the surface of the C3S particles. This view is supported by Kawashima et al. (2013) who provided a basis for understanding the mechanical properties of high-volume fly ash when incorporated with nano-CaCO₃. It was shown that the addition of 5% nano-CaCO₃ with 30% fly ash-cement paste samples tested at 1, 3 and 7 days showed progressive development in compressive strength compared to control fly ash- cement paste [12,13]. Oil well cement (OWC), a kind of special cement-based materials, have relatively high compressive strengths but sensitive to tensile stresses inevitably. In the petroleum industry, OWC is typically utilized to fill the annular space between the pipe and rock formation, displaces the drilling fluids, support the casing and protect it against corrosion and impact loading, restricts the movement of fluids between formations, and isolates the productive and none productive zones [14,15]. The cement must withstand higher pressures and also resist more corrosive fluid attacks encountered in down hole applications [16]. Therefore, to improve the strength while maintaining higher ductility is a challenging task for possible application of OWC. 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) [17]. Also OWCs are classified into three grades based upon their C₃A contents [18]. At present, a common approach to reduce the brittleness is blending with various reinforcing additives such as fibers, nano-sized particles of different types of cement admixtures which enhance OWC slurry properties, to achieve successful placement and rapid compressive strength development for adequate zonal isolation during the lifetime of the well and enhance mechanical properties by decreasing the micro-porosity of nano-sized particles and reducing the crack propagation [19,20]. Therefore, the aims of this study was to prepare and evaluate the effects of ESNP as a novel reinforcing additive on mechanical properties development and microstructure of OWC.

![Fig.1 Schematic description of accelerating effect of addition of nano-CaCO₃ on hydration of C³S.](image)

2. Materials and methods
2.1. Preparation of eggshells nanoparticles (ESNP)
In this study raw eggshell was collected from a kitchen home and immediately, were rinsed with clean water to remove the residue egg contains that attached on the egg shells. After that, it was dried in an oven at 70°C for 30 min. to remove water content. The clean eggshells were pretreated by home grinder to obtain eggshell micro-particles (ESMP). The powder obtained were sieved to 300 µm sieve using a Sieve Shaker, micro-particles were then placed into the ball mill simultaneously with the grinding balls for a period of 5 hr., then powders was sent to mesh for the size lower than 300 µm in order to remove severe clusters that originated during milling process. The fraction was dried again in an oven at 70 °C for 30 min as shown in Fig.2. which represents the practical steps of preparation ball-milled eggshells nanoparticles. After 5 hour-milling; the ball-milled eggshells were tested using particle size analyzer (Malvern Instruments Master size 2000) to detect the particle size distribution. The meshing, drying and (PSA) are frequently done in every 5 h of milling while attaining the total time of 30 h. The mesh sizes employed were 600 µm, 300 µm, 140 µm, and 100 µm. The resulting powder was milled in a ball-milling machine (GW, Korea) for 5, 10, 15, 20, 25 and 30 h at a speed of 170 rpm. The crystalline phases of the ball-milled powders before and after the mechanical treatment were analyzed by using X-ray diffraction (XRD-6000, Shimadzu). The microstructure and morphology of the powders were studied using scanning electron microscope (SEM; JSM-6700F, JEOL, Japan). The composition of the prepared powders was analyzed by X-ray fluorescence spectrometry (Shimadzu XRF-1800). The chemical compositions and physical properties of eggshell nanoparticles of ESNP are summarized in Table 1.
2.2. Mixing and preparing cement slurry of (OWC)
Cement slurries used in this study were prepared using oil well cement API Class G with a specific gravity of 3.14. Deionized distilled water was used for the mixing with a $w/c = 0.44$, and its temperature was maintained at $23\pm 1^\circ C$ using an isothermal container. The cement slurries were prepared using a high-shear blender type mixer running at a speed of 4000 r/min ± 250 r/min. with bottom driven blades according to the following procedure. First, the weighted amount of cement and the solid admixture (ESNP) in three concentrations (2% ,6% and 10%) were dry mixed in a bowl by hand using a spatula for about 30 sec. The mixing water was subsequently poured into the blender. The mixing started at a slow speed for 20 sec. Manual mixing was conducted for 20 sec and a rubber spatula was used to remove material sticking to the wall of the mixing container to ensure homogeneity. Finally, mixing resumed for another 35 sec at high speed. This mixing procedure was strictly followed for all cement slurries. All mixing was conducted at a controlled ambient room temperature of $23\pm 1^\circ C$. All the abbreviations are shown in Table 1. The chemical compositions and physical properties of Oil well cement API Class G, and eggshell nanoparticles are given in Table 2 A and B.

Table 1. Abbreviations

| Symbols | Meaning |
|---------|---------|
| ESNP | Eggshell nanoparticles |
| ESNP2(40) | Eggshell nanoparticles according to the particle size analyzer for this group, higher than 40nm with 2% nanoparticles. |
| OWC | Oil Well Cement |
| CM | Control mixture |
| C–S–H | Calcium silicate hydrate |
| w/c | water-to-cementitious materials ratio |

Table 2. The chemical compositions and physical properties of OWC and ESNP.

| Chemical Component (%) | Oxides | Wt.% |
|------------------------|--------|------|
| CaO | 64.20 |
| SiO₂ | 19.40 |
| Fe₂O₃ | 5.50 |
| Al₂O₃ | 4.50 |
| SO₃ | 2.80 |
| MgO | 2.00 |
| Na₂O | 0.10 |
| K₂O | 0.60 |
| C2S | 15 |
2.3. Specimen preparation, curing, and testing
The specification gives the standard procedure for sample condition prior testing. The slurries prepared according to API RP (10B-2) standard were placed in the moulds sized (2in x 2in x 2in) in a layer equal to half of mold depth and puddle for 25 times per specimen with pudding rod. The prepared slurries were placed in all specimen compartments before commenced the pudding operation. After pudding the layer, the remaining slurries was stirred using pudding rod and strike off the excess slurries on the mould top using a straight edge. The dry cover plate was placed on the mould top before the sample was ready for curing process. Table 3. Shows mixing proportion of prepared OWC samples. The specifications of equipment's used during this work have been given in Table 4.

Table 3. Mixing proportion of cement samples.

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

Table 4. Specifications of equipment’s used.

| Equipment                                      | Specification                                    |
|------------------------------------------------|-------------------------------------------------|
| Ball mill                                      | (GW, Korea) 250 rpm                              |
| Mechanical Shaker, Heidolph                    | UNIMAX 1010/PROMAX 1020, Germany                |
| Ultrasonic                                     | 750 Watt Ultrasonic Processors – VCX Series      |
| Electrical furnace                            | Hanna 211, Romania                               |
|                                               | Electrical furnace (20–500) °C                   |
| X-ray fluorescence spectrometry               | Shimadzu 1800                                   |
| Mixer for preparation cement slurry            | High speed mixer – 4000 rpm                      |
| Particle Size Analyzers (PSA)                  | Malvern Mastersizer 2000                        |
| Brunauer, Emmett and Teller (BET) method       | Q Surf 1600, USA                                 |
| Atomic Force Microscope (AFM)                  | Angstrom, Scanning Probe Microscope, Advanced Inc., AA 3000A, USA |
3. Results and discussion

3.1 Characterization of ball-milled powders ESNP

As presented in Table 1, the chemical composition of the ESNP from the X-ray fluorescence (XRF) shows that calcium oxide (CaO) was the most abundant component (97.8%). The high amount of (CaO) is associated to the presence of calcium carbonate, which is the main component of eggshell. Thus, the eggshell waste sample can be considered from a chemical viewpoint a pure relatively natural carbonate-based material, as well as its composition is very similar to that of calcitic calcareous. Scanning electron microscope images of eggshell micro-particles (ESMP) and eggshell nanoparticles (ESNP) are presented in Fig. 3. The SEM images shown in Fig. 3A illustrate morphology, texture, size and distribution of the ball-milled eggshell (ESMP) after 5 h of milling. It can be seen that some of ESMP particulates which have fused together resulted from constricting action of the ball-milling process were irregular in shape and their surface was rough. Furthermore, the diameter varied greatly, ranging from 0.7 µm to 10 µm. Conversely, the SEM images shown in Fig. 3B demonstrate ball-milled eggshell nanoparticles after 25 h of milling, different structures of the particles including oval and irregular shaped particles as well as agglomerates are due to constricting action of the ball-milling process with sizes ranging from 40 nm to 110 nm. As it can be visually perceived from the results the ESNP is not homogeneous and several primary particles seem to cluster or fuse at their faces. This tendency for agglomeration in the particles is induced by the Van-der-Waals forces acting between the individual particles. The purity and crystallinity of ESMP and ESNP were analyzed using X-ray diffraction (XRD) as illustrated in Fig. 4A and B which demonstrate the structural changes and degradation of the ball-milled eggshell after mechanical treatment for 25 hr., compared with mechanical treatment for 5 hr. XRD profile in Fig. 4A shows that, the pattern of calcite (CaCO$_3$), and demonstrates the presence of a large amount of highly crystalline calcite. The (012) and (104) basal reflections, initially are very strong, a decrease in intensity after bash is shown in Fig. 4B. The reflections (110), (113) and (202) decrease too, but are different from others after mechanical treatment for 25 h. This confirms the structural changes in the treated calcite (ESNP) compared to the ESMP. The distortion of structure is reflected in the line vacillation, in the decrease of peak intensity (area) and in the shifting of reflections. The losses of the crystallinity in the basal diffractions are due to the amorphization phenomenon. The eggshell powder obtained from mechanical treatment were verified by particle size analyzer instruments to evaluate particle size and size distribution during milling process. According to PSA and AFM results the eggshell powder has successfully been reduced the particle size to 40 nm within 25 hr. The size distribution of particles was in six main different size categories as shown in Table 5, Fig. 5 and Fig. 6. Based on the milling pattern, it can be concluded that the mineral is brittle and can be characterized by reduction in particle size at first and then by agglomeration (clumping) on increasing the milling time. Agglomeration is the result of Van der Waals forces between particles at the surface.
Table 5 The average particle size of milled eggshell with milling time.

| Groups  | Milling Time (h) | Particle size group | Average particle size (nm) |
|---------|------------------|---------------------|-----------------------------|
| ESNP1   | 5                | (0.7-20) µm         | 500                         |
| ESNP2   | 10               | (200-350) nm        | 170                         |
| ESNP3   | 15               | (130-170) nm        | 90                          |
| ESNP4   | 20               | (90-120) nm         | 60                          |
| ESNP5   | 25               | (40-110) nm         | 40                          |
| ESNP6   | 30               | (50-150) nm         | 70                          |

![Fig. 3](image_url) SEM images of (A) eggshell microparticles (B) eggshell nanoparticles.
**Fig. 4.** X-ray diffraction patterns of (A) eggshells micro-powder and (B) eggshells nano-powder.

**Fig. 5.** Particle size analyzer of prepared eggshell nanoparticles after 25h of milling.
3.2. Characterization and analysis of OWC

3.2.1. SEM observations and microstructural analysis of control mixture

**Fig. 8A** shows the SEM micrographs of the OWC control mixture (CM) at the age of 8 h. at 60 °C and demonstrates the porous structure which is full of large size pores and the presence of Ca(OH)₂ or (CH) that is over-shadowed. Also, it can be seen from the same figures that the CH crystals are connected to the C–S–H gel which indicates that the hydration process is not completed and also explains the low records of compressive
strength for the control mixtures. Also, the same photos show that the concentration of the CH is higher than the C–S–H gel concentration and that the CH hydrate needles cover a large area.

3.2.2 SEM observations and microstructure analysis of modified OWC

The SEM images of the OWC mixture after incorporating 6% of ESNP are shown in Fig.8B that was prepared with nominal particle size group of 40-110 nm. The images show that the microstructure of the mixture after incorporating ESNP at 8h and 60 °C is dense and more organized with a small number of Ca(OH)₂ crystals and small sized pores while in the control mixture the C–S–H gel existed in the form of clusters lapped and joined together by many CH needles hydrates. It can also be noticed from the reference figure that the CH needles are visible and there is a compact structure with the absence of the unhydrated crystals and voids. The structure is more uniform and homogeneous than that of the CM sample which explains the superior compressive strength results. This could be due to the high activity of many particles that promote the pozzolanic reaction to produce more C–S–H gel in order to reach high compressive strength at an early age which is confirmed by the strength results. The CaCO₃ nanoparticles consumes calcium hydroxide crystals, fills pores to increase the strength, reduces the size of the crystals at the interface zone and transmutes the calcium hydroxide feeble crystals to the C–S–H crystals, and improves the interfacial zone and cement paste structures.
3.2.3 X-ray diffraction of OWC

XRD analyses were conducted to investigate the activity and potential of incorporating ESNPs on selective OWC specimens after 8h of hydration. The samples were cured for 8h of hydration and 60 °C before being subjected to XRD technique. It is obvious from XRD profiles that the CH peak is almost decreased with the addition of NP, while the same is significantly present in the control mixture. It is therefore inferred from Fig. 9A and B that, the NPs reacts with CH produced during the hydration process. The pozzolanic reactivity of NP at early stage of hydration is significantly high and improves the microstructure of cementitious system, thereby enhancing the mechanical properties of the cementitious materials. For comparison, the peaks of CH at 2Θ =18 and 47 have been selected as shown in Fig. 9A. A sharp peak in CH is observed in the control mixture representing the pure hydration product (CH), which is released from the hydration of cement. Evidently, the intensity of the CH peak is decreased due to adding NPs as a cement replacement, which reflects the consumption of CH by pozzolanic reaction as shown in Fig. 9B. In agreement with the SEM results, which explain the absence of the unhydrated crystals (needles) and voids, in addition, more uniform and homogeneous mixtures have been obtained than from the CM sample.
3.3 Compressive strength development

All specimens were prepared with minimum particle size group (40-110 nm) due to impact of the particle size on strength development. The minimum particle size of NPs increases the packing efficiency decreases leading to a drop in the compressive strength.

3.3.1 Effect of ESNP dosage on compressive strength

Compressive strength development of the OWC incorporating different dosages of ESNP is given in Table 6. In comparison with that of CM, the modified OWC with NPs had exhibited higher compressive strengths. However, the strength of the samples increased with the increase in NPs concentration to best value up to 60°C. By examining the strength of the OWC prepared in different percentages of NPs for the same particle size, it can be seen from Fig. 10, that mixtures having 6% ESNP content displays higher compressive strength than their counterparts prepared with low NPs percentage. For example, the mixture with NPs of nominal particle size 40 nm exhibited a compressive strength of 3.61 MPa at 38°C and 6% NPs, while it recorded 2.7 MPa at 2% NPs at the same age and temperature. Conversely, a different observation was detected for mixtures which incorporated NPs where the compressive strength result at 6% ESNP content and temperature of 60°C was 12.46 MPa, while slumped to 12.11 MPa at 10% of NPs. This means that on increasing the percentage of NPs is useful in increasing strength to a certain limit after which any increase in the NPs content leads to a decrease in the compressive strength.

Table 6. Compressive strength with different percentage of ESNPs

| Test                          | Without Additives | With Additives |
|-------------------------------|-------------------|----------------|
|                               | CM (0%)           | 2%  | 6%  | 10% |
| Compressive strength in (MPa) | 2.50              | 2.70 | 3.61| 3.53|
3.4 Effect of ESNP on rapid chloride permeability (RCP) of OWC
All the OWC mixtures result with NPs were less permeable to chloride penetration than the CM, which indicates that adding NPs to OWC mixtures decreases their permeability. For instance, it can be depicted from Table 6 that the CM recorded charges of 5307 coulombs which dropped to 3411 coulombs for the mixture ESNP2(40) and further decreased to 590 coulombs with the ESNP6(40) mixture. Also, it shows that increasing the percentage of NPs in the mixture, decreases its permeability which matches the results of compressive strength test. For example, the mixture ESNP2(40) produced with 2% NPs reached high permeability charges 3411 coulombs which makes it moderately permeable while the mixture ESNP4(40) produced with 6% NPs of the same nominal particle size displayed less charges of 600 coulombs which is classified as very low permeable. The test results are shown in Fig.11 and listed in Table 7. In conclusion, the RCP decreases with adding CaCO3 nanoparticles. It can also be concluded that the permeability of OWC mixtures decreases with the increase in the NPs content added to the mixture due to the effect of packing efficiency of the voids and cavities.
Table 7. Rapid chloride permeability test results.

| Mixture I.D.     | Cell No. | Charges passed (Columbus) | Permeability class |
|------------------|----------|---------------------------|--------------------|
| CM               | 1        | 5307                      | high               |
| ESNP2(40)        | 2        | 3411                      | moderate           |
| ESNP6(40)        | 3        | 600                       | very low           |
| ESNP10(40)       | 4        | 590                       | very low           |

Fig. 11. Chloride ion permeability resistance of different concretes measured.

4. Conclusions

From this work, the following main conclusions are drawn.

- CaCO$_3$ nanoparticles was successfully obtained by ball milling method for 25 h with average particle size of 40 nm.
- The characterization of CaCO$_3$ nanoparticles shows spherical particles and those have irregular shapes as well as agglomerates fuse together and the range of external diameters is in the 40-110 nm range.
- Incorporating CaCO$_3$ nanoparticles into OWC mixtures enhances their mechanical properties and performance by yielding higher compressive strengths than the control mixture exhibiting relatively high early strengths and resisting the acidity.
- Within the particle size range 40-110 nm and dosage range studied the compressive strength generally increased with the addition of CaCO$_3$ nanoparticles. The addition of NPs in 6% at 40 nm particle size gives the highest the compressive strength for the OWC mixtures.
- The results supported the notion that the CaCO$_3$ nanoparticles act not only as filler, but also as an activator to support the hydration process. The presence of CaCO$_3$ nanoparticles increases the reaction rate of tricalcium aluminate (C3A) to form carboaluminate complex thereby increases the total hydration products and delays the formation of micro-cracks, and the hydration products and consequently the compressive strength. In addition, it also
reacts with tricalcium silicate (C3S) and accelerates setting and early strength development.

References

[1] M.C.M. Nasvi, P.G. Ranjith, J. Sanjayan, A numerical study of triaxial mechanical behaviour of geopolymer at different curing temperatures: an application for geological sequestration wells, J. Nat. Gas Sci. Eng. 26, 1148–1160, 2015.

[2] J. Won, D. Lee, K. Na, I.-M. Lee, H. Choi, Physical properties of G-class cement for geothermal well cementing in South Korea, Renewable Energy 80, 123–131, 2015.

[3] C. Ma, L. Chen, B. Chen, Analysis of strength development in soft clay stabilized with cement-based stabilizer, Constr. Build. Mater. 71, 354–362, 2014.

[4] C. Ma, B. Chen, Properties of a foamed concrete with soil as filler, Constr. Build. Mater. 76, 61–69, 2015.

[5] W. Khalilq, H.A. Khan, High temperature material properties of calcium aluminate cement concrete, Constr. Build. Mater. 94, 475–487, 2015.

[6] A. Brandl, J. Cutler, A. Seholm, M. Sansil, G. Braun, A. Brandl, et al., Cementing solutions for corrosive well environments, Spe Drill. Complet. 26 (2), 208–219, 2011.

[7] Najat J. Saleh, Raheek I. Ibrahim, Ali D. Salman. Characterization of nano-silica prepared from local silica sand and its application in cement mortar using optimization technique. Advanced Powder Technology 26, 1123–1133, 2015.

[8] M.A. Caldarone, K.A. Gruber, R.G. Burg, Highreactivity metakaolin: a new generation mineral admixture, Concr. Int. 16, 1994.

[9] M.H. Zhang, V.M. Malhotra, Characteristics of a thermally activated aluminosilicate pozzolanic material and its use in concrete, Cem. Concr. Res. 25 (8), 1713–1725, 1995.

[10] F. Wang, S. Wang, Y. Meng, L. Zhang, Q. Wu, J. Hao, Mechanisms and roles of fly ash compositions on the adsorption and oxidation of mercury in flue gas from coal combustion, Fuel 163, 232–239, 2016.

[11] S.V. Vassilev, C.G. Vassileva, V.S. Vassilev, Advantages and disadvantages of composition and properties of biomass in comparison with coal: an overview, Fuel 158, 330–350, 2015.

[12] Najat J. Saleh, Raheek I. Ibrahim, Ali D. Salman. Optimization Process for Using Prepared Nano silica in Concrete. The 2nd International Conference of Buildings, Construction and Environmental Engineering, BCEE2-2015.

[13] M.R. Shatat, Hydration behavior and mechanical properties of blended cement containing various amounts of rice husk ash in presence of metakaolin, Arab. J. Chem., 2013.

[14] M.S. Morsy, Y.A. Al-Salloum, H. Abbas, S.H. Alsayed, Behavior of blended cement mortars containing nano-metakaolin at elevated temperatures, Constr. Build. Mater. 35, 900–905, 2012.

[15] Wu, Z.; Shi, C.; Khayat, K.H. Multi-scale investigation of microstructure, fiber pullout behavior, and mechanical properties of ultra-high-performance concrete with nano-CaCO3 particles. Cem. Concr. Compos. 2018, 86, 255–265.

[16] Ge, Z.; Wang, K.; Sun, R.; Huang, D.; Hu, Y. Properties of self-consolidating concrete containing nano-CaCO3. J. Sustain. Cement-Based Mater. 2014, 3, 191–200.
[17] Yang, H.; Che, Y.; Leng, F. High volume fly ash mortar containing nano-calcium carbonate as a sustainable cementitious material: microstructure and strength development. Sci. Rep. 2018, 8, 16439.

[18] Ge, Z.; Wang, K.; Sun, R.; Huang, D.; Hu, Y. Properties of self-consolidating concrete containing nano-CaCO3. J. Sustain. Cement-Based Mater. 2014, 3, 191–200.

[19] American Petroleum Institute. Recomended practice for Testing Well Cements, API Spec.10 B 1st edition, American Petroleum Institute, Washington DC (2010).

[20] Kim D H, Park C G. Strength, permeability, and durability of hybrid fiber-reinforced concrete containing styrene butadiene latex. Journal of Applied Polymer Science, 2013, 129(3): 1499–1505.