Producing a new type of cement by adding Zirconium Oxide

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Abstract. Concrete is one of the important ingredient in the field of construction, this concrete can improved by adding some extra additives like nano powders which helps to increases the strength of concrete, but neon powder of zirconium oxide is very useful for reducing temperature effects and high hardness property, so it used in a high temperature condition as a coatings and paints, the requirement of journals by using nano zirconium oxide powder in concrete is minimum. In this present work nano zirconium oxide used as energy enhances to increase the strength of the concrete, nano zirconium oxide powder is added into the concrete with different percentage of 0%, 0.25%, 0.5%, 0.75%, 1.0%, 1.25%, 1.5%, 1.75 and 2.0%, which are mixed separately for each specimen with water and 0.5 kg for 100 kg binder (cement-ZrO₂) of superplasticizer glenium 51 is mixed by using mixer for 2 min. in order to get the uniform dispersion of nano powder in the mortar and after adding (50-70)% of the water to be added to the mixture, the specimens with nano zirconium oxide gives the high compressive, tensile, hardness strength when compared to normal mortar at each different percentage of nano zirconium oxide and it increases the strength after 90 days.

1. Introduction
Mortar basically consisted of cement, sand and water. Ordinary Portland Cement (OPC) plays a very important role as binder in mortar. Mortar with cement replacement of mineral or pozzolanic admixtures is called modified mortar the partial replacement form cement content can improve the durability of the mortar produced. According to Zhang and Li (2011) [1], effective dispersion of nanoparticles is considered the significant problem in the use them in concrete due to pore size of concrete containing nano-ZrO₂ is much smaller than other concrete having the same quantity of nano-SiO₂. Nazari et al. (2011) [2] used 15 nm nano-particles of TiO₂ and they stated an enhancement up to 4% in the flexural strength of self-consolidation concrete. However, due to poor dispersion of nano-particles within the concrete, content increasing of nano-particle lead to a reduction in flexural strength. Nochaiya et al. (2011) [3] obtained a homogeneous dispersion of nano-particles in concrete when they mixed the nano-particles with water and exposed the mixture for one hour under the ultrasound. Metaxa et al. (2012) [4] produced very concentrated suspensions of carbon nano-tubes by developing an ultra-centrifugation concentration process. In this research, the effect of ZrO₂ nano-particles on flexural strength and compressive strength of cement mortar has been studied. Calcium hydroxide Ca(OH)₂ formed from the calcium silicates hydration interact with the ZrO₂ nano-materials. Surface area of the reaction is proportional to the rate of the pozzolanic reaction. So, adding high purity (99.9%) and a high Blaine fineness value (60) (m²/g) of ZrO₂ nano-particles is important to enhance the mechanical properties of cement mortars [5]. In our research, we obtained a high strength concrete (HSC) or a high performance concrete (HPC) with small increase in price by using new materials.
HSC and HPC are widely used in constructions and towering buildings due to decrease of the cross-sectional area of the structural fundamentals.

2. Materials and mixture of the work:

2.1. Materials:

2.1.1 Nano Zirconium Oxide powder (ZrO₂):
Nano–ZrO₂ with average particles size of 15 nm was acquired from (NANOSHEL-INTELLIGEN MATERIALS PVT. LTD); company/ USA [6] has used as received. Tables (1) and (2) show the physical and chemical properties of ZrO₂ nano-particles.

| Sl.no. | Physical Properties   | Zirconium oxide |
|-------|-----------------------|-----------------|
| 1     | Purity                | 99.9%           |
| 2     | APS                   | 40nm            |
| 3     | SSA                   | 30-40 m²/g.     |
| 4     | Appearance            | White           |
| 5     | True density          | 5.68 g/cm³      |
| 6     | Crystal               | Monoclinic      |
| 7     | Melting point         | 2715 °C.        |

Table 1. The physical properties of ZrO₂ nano-particles [6]

| Sl.no. | ZrO₂ | Al₂O₃ | SiO₂ | Fe₂O₃ | TiO₂ | Cl      |
|--------|------|-------|------|-------|------|--------|
| 1      | 99.9%| <0.026%| <0.005%| <0.06%| <0.03%| <0.05% |

Table 2. The Chemical properties of nano-ZrO₂ [6]

2.1.2. Cement:
Ordinary Portland Cement (OPC) type I- its name (MASS) fabricated from Al-Sulaimaniyah city in the north of Iraq was used in this study. The physical and chemical analysis where carried out by the National Centre for Laboratories and Construction Research. The test results show that the Ordinary Portland Cement abided by the Iraqi standard specification (L.O.I.S.) No. 5 / 1984 [7]. Table (3) shows the physical properties and chemical compositions of OPC.

| Item   | % by weight | specification Limit according to (L.O.I.S) No.5:1984 |
|--------|-------------|------------------------------------------------------|
| SiO₂   | 19.5        | -                                                    |
| Fe₂O₃  | 3.8         | -                                                    |
|                | Comp | MgO  | 2.25  | <5.00 |
|----------------|------|------|-------|-------|
|                |       | CaO  | 61.34 | -     |
|                |       | Al₂O₃| 4.79  | -     |
|                |       | SO₃  | 1.33  | <2.80 |
| Time saturation factor (T.S.F.) | 0.85 | 0.66 – 1.02 |
| Insoluble residue (I.R.) | 0.97 | <1.5 |
| Loss on ignition (L.O.I.) | 1.41 | <4  |

Physical Properties

Compressive strength of (70.7) mm cement mortar cube (MPa)

|       | Test result |
|-------|-------------|
| 7 days | 24.54 >23   |
| 3 days | 17.15 >15   |

Setting time (Vicat’s method)

|                     |                |
|---------------------|----------------|
| Final setting (min) | 275 <10 hrs.   |
| Initial setting (min)| 148 >45 min   |

Fineness (cm²/g) by Blaine method

|                       |                |
|-----------------------|----------------|
| Soundness using Auto; clave% | 0.25 <0.8 |

2.1.3. Fine aggregate:
Natural sand with diameter of a smaller than 4.75 mm was used in current research. Its fineness modulus (F.M.) is 2.60. Locally available from AL–Ukhaider, Karbala, Iraq. Sulfate content (SO₃%) and bulk specific gravity (S.G.) is (0.09%) and (2.58) respectively by weight of sand. This limit followed the Iraqi standard specification No. 45 / 1984 [8].

2.1.4. Glenium 51
Glenium 51 is polycarboxylic based ether with a high range reduction of water and new second generation of superplasticizer concrete admixture established for mixed concrete and precast industry which high early, final strengths and durability are needed. The technical description is given in table (4) [9].

| Basis;                      | Modified polycarboxylic ether |
|-----------------------------|-------------------------------|
| Appearance                  | Light brown / vicious liquid  |
| Specific gravity            | 1.1 at 20°C                   |
| Viscosity                   | 128±30cps @ 20°C              |
| PH                          | 6.6                           |
| Labeling                    | Not hazard label required     |
| Transport                   | Not classified as dangerous   |
| Storage                     | Has to be stored in original  |
|                             | Containers and at temperature above 5°C |

2.2. Mixture:
In the laboratory trials, two main types of the mixtures contain were constructed. First type of mixtures (CM) was constructed as control specimens. (CM0) are the control mixtures which are made of water, cement, and sand (without ZrO₂ Nano materials). (NM) mixtures are the second types were constructed with different amount of ZrO₂ nano-particles with a 15 nm average particle size. The specimens were prepared with replacement of the cement of 1.75%, 1.25%, 0.75%, and 0.25%, by weight. The (sand / cement) ratio was determined at (3:1) for all mixtures, and the ratio of (water/binder) ratio was determined at (0.5%). Table (4) presented the mixtures proportions [10].

| Groups name | Cement content % | Nano-particle ZrO₂% | (water/cement) % | (sand/cement) ratio |
|-------------|------------------|---------------------|------------------|---------------------|
| CM0         | 100              | 0                   | 0.5              | 3:1                 |
| NM1         | 99.75            | 0.25                | 0.5              | 3:1                 |
| NM2         | 99.50            | 0.5                 | 0.5              | 3:1                 |
| NM3         | 99.25            | 0.75                | 0.5              | 3:1                 |
| NM4         | 99.00            | 1.00                | 0.5              | 3:1                 |
| NM5         | 98.75            | 1.25                | 0.5              | 3:1                 |
| NM6         | 98.50            | 1.50                | 0.5              | 3:1                 |
| NM7         | 98.25            | 1.75                | 0.5              | 3:1                 |
| NM8         | 98.00            | 2.00                | 0.5              | 3:1                 |

3. Specimens Preparation:

3.1. Work Procedure:
The equipment of mixtures was carried out similar to ASTM C 305-12 [10] with some variations:
- The sensitive digital balance was used for weighing components of 0.01 gm and for ZrO₂ nano-particles and another one of 0.0001 gm digits.
- The mixture without Nano-particles of ZrO₂, sand and cement were manually mixed until they reached to a homogeneous form and the electrical mixer was used to mix the mixture of cement and sand together with the water for 3 min and the last step of mechanical mixing.
- When the mixtures were contained ZrO₂ nano-particles, 95% of the total water was added to the mixture and was mixed by hand for 5 min. Then all of the mixture was sonicated for 20 min. to get a well dispersion of ZrO₂ nano-particles and for a better homogenization of the mixture [11]. The ultrasonic wave path machine model (LUC) (220 V, 50 Hz, 400 W) (Power Sonic 410) was used.
- Accommodate sand and cement which previously mixed together in the mixer, with the mixture that contained nano-ZrO₂ and water.
- 5% of water must be added slowly after 60 sec. of mixing, and mixing was kept for additional 30 sec.
- The mixer was kept for 90 sec. for rest after stopping, and then mixed again for 90 sec.
- The mortar that extracted from the mixer was poured into the oiled, clean molds. The densification of the specimens was prepared in two layers by using a vibrating machine that each layer vibrated for 10 sec. [12]. Then finishing the surface of the samples.
• Then, plastic sheets were used to cover the molds to protect the mixture from the moisture content and the samples were kept in laboratory for 24 hours at the temperature of (24±1 Co).
• Then the specimens were de-molded and cured in water where they should be remained till the age of test.
• Glenium 51 was added to all mixes with a ratio of 0.8 kg of 100 kg of binder (cement-ZrO₂) after adding (50%-70%) from the mixing water.

3.2. Compressive strength:
Compressive strength test was done following ASTM C109-02 that was fulfilled [13]. for each mixture, the compressive strength was calculated from an average of three cubic samples (50 × 50 × 50)mm at the age of 7, 14, 28 and 90 days of curing.

3.3. Flexural strength:
Following the ASTM C 293-03 the flexural strength test was fulfilled [14]. For each mixture the flexural strength was caused from an average of three specimens (160 × 40 × 40) mm at the age of 7, 14, 28 and 90 days of curing. Compression test and flexural test were carried out utilizing Universal Mechanical test machine, TINIUS OISEN H50KT for Compression, Flexural (Bending) strength and Tensile strength tests at Materials Engineering Department / Mustansiriyah University in Material Testing Laboratory.

3.4. Density Test
At the end of each curing age (7, 14, 28 and 90 days respectively), the mortar cubes were detached from the tank of curing and allowed to drain off. The weight of each cube was gained by a weighing balance to set the density of the mortar cube [15]. Equation (1) was used to obtain the density of each cube.

\[
\text{Density} \ (\rho) = \frac{\text{weight of cube}}{\text{volume of cube}} \ (\text{Kg/m}^3) \quad \text{………………… (1)}
\]

3.5 Water absorption
The forces of capillary are measured by the water absorption test due to the force given to the capillary forces, the minute opening of the structure causes amounts of fluids that are rushed in the physical structure of the material. The total quantity of water soaked up by mortar mixes contains tightness of water and the impeding effects of the mixes. The mixes are prone and affected by the water absorption test in the final part of the treatment within the periods of 7, 14, 28 and 90 days after the process of dismantling, removing, reassembling, and finally repositioning. A treatment tank is used to contain the mixes two days before the period of testing and then an oven is used to be preserved by evaporating the moisture from at 100±5°C in a period of seven days. This process is done when after the competition the constant mass and the weight of each sample used. The wax will be used to cover all the areas of the samples the samples were covered with wax other than its lowest point before being submerged in flat and shallow containers having water. The cube is covered with wax in order to keep it from the entrance of air when submerged in water. Since the cube is not fully soak in water, but only about (30-35) mm of water level the start time was immediately recorded. after 7 days the samples were removed from the tank, shook to remove bulk of the water, and dried with a cloth as fast as possible to remove all free water on the surface. They were then weighed again. The measured water absorption of each samples were expressed as the increase in the mass percentage of the oven dry mass [15].

3.6 Shore hardness (ASTM D-2240)
Shore hardness is a standard unit of measuring hardness and it is noticed from the name of the term There is a variety of the methods used in the tests whether in the field test or the laboratory one. The tests made with the given results rely on the arrangement of parts and elements in a particular form and figure of the sample having level surface. More importantly, particular persons having gained
knowledge and skill should do the testing working together with an expert who represents the manufacturers' field. The equipment of the Field measuring devices can be gained from different people who trade in these devices. The shore "D" Durometer is utilized to measure the hardness of harder materials such as rigid epoxy based materials. Both scales are from 0 to 100, hence a unit to unit correlation is not always possible dependent upon the particular hardness of the material being measured [16].

3.7 Ultrasonic pulse velocity (UPV)
Ultrasonic pulse velocity test was performed based on ASTM C597-02 [17] where MATEST is used and is easily moved and carried. Measuring the speed of the pulse in the samples of mortar is gained by the frequency given by the devices that convert variations in a physical quantity called transducers. This is done in 54 KHz. Test is also made on the samples of cubes with dimensions (50x50x50) mm. Grease is used to cover the transducers to provide good connection. The level of the equipment is examined many times and instrument setting was checked frequently by the person who test provided with reference bar. An alteration is done to the zero reference slightly in order to achieve the desired result of the agreement between the display transit time with the bar value (42.5 µm). The direct transmission method was used in the in the instrument in order to get absolute value of elasticity (E_d) of constant change and activity as well as to get compressive strength. The speed of the pulse is evaluated by the test and is calculated from the equation as follows (2):

\[ V = \frac{L}{T} \]  

Where:
T= Transit time, (sec).
L= Distance between the center of transducer face, (m).
V= Pulse velocity (km/sec.)

3.8. SEM analyses samples:
After completing the mechanical test for samples of 28-day curing, SEM test was used to study the microstructure of broken pieces of the samples. By employing the means of VEGA3/ Tescan SEM device, this test is used in the Nanotechnology Laboratory in the Materials Engineering Department / Mustansiriyah University.

4. Results and Discussion:

4.1. Mechanical properties:
The three trials used in the test of this study represent the average values. The discussion of the results is covered in the following sections.

4.1.1. Compressive strength test:
Figure (1) shows the results of compressive strength for all the combination of the mixed components. By comparing together the findings of the samples done within 7, 14, 28 and 90 days, it has been demonstrated that the compressive strength increases with nano-ZrO₂ particles reaching up to 1.25% replacement (NM5). The compressive strength decreases after that. Although the compressive strength has 2.0% replacement (NM8), this percentage is higher than the ones in the normal cement mortar (CM0). Based on the results, there is closeness between the reduction of the normal cement mortar (CM0) and the reduction observed in the compressive strength of (NM8). Perhaps, this is due to the inefficient ways in which nano-ZrO₂ are distributed and they may leave areas lacking strength. Additionally, the total number of the nano-ZrO₂ particles needed to be merged with the released lime is less than that the ones found in the mixture throughout the duration of hydration. Hence, this leads to two things: spare silica draining away and strength absence that takes the place of the material made from cement. However, it does not help to provide strength.
The reason behind the high increasing in compressive strength of the NM additives, especially at the early time in relation to the great reactivity found in nano-ZrO$_2$ is quick consumption of Ca(OH)$_2$ that is shaped in the hydration process of Portland cement. Therefore, the amount of reaction substances is slower and less effective than the cement hydration. The degree of compactness of the particle packing is removed by nano-ZrO$_2$ particles in the mixed cement and these results in reduced amount of greater minute openings in the cement mixture.

![Compressive strength graph](image)

**Figure 1.** ZrO$_2$ (%) and compressive strength (Mpa.) relationship.

### 4.1.2. Flexural strength test:

Figure (2) shows the results of the flexural strength of CM0 and NM of mixed substances. The bending and compressive strength of the samples has an increase in nano-ZrO$_2$ particles and the percentage of this increase is 1.25% replacements (NM5) like the one found in the compressive strength. This increase then declines in spite of the results gained which is 2.0% replacement (NM8) and is greater than the ones found in the normal cement mortar (CM0). The quick absorption of the energy of Ca(OH)$_2$ causes the flexural strength. The consumption is created within the hydration process of Portland cement at the early times accompanied with great amount of reactivity in nano-ZrO$_2$ particles.
4.1.3. Density test:
Figure (3) shows the results of the density for both CM0 and MN mixtures. The results have shown an increase with nano-ZrO$_2$ particles up to 1.25% replacement (NM5) like the compressive strength. Of 2.0% replacement (NM8) has higher density than the normal cement mortar (CM0), the samples show a remarkable decrease.

4.1.4. Absorption test:
Figure (4) shows the absorption results of the test for CM0 and MN mixtures and they decrease by adding nano-ZrO$_2$ particles up to 1.25% replacement of cement (NM5). The absorptions results then increase, despite the fact that results of 2.0% replacement (NM8) has lower absorption than the normal cement mortar (CM0).
4.1.5. Hardness (shore D) test:
The results of the hardness test of the CM0 and MN mixtures are illustrated in figure (5). As found in the compressive strength of the samples, the hardness increases by adding nano-ZrO\textsubscript{2} particles up to 1.25\% replacement (NM5). Then, the hardness decreases, despite the fact that the results of 2.0\% replacement (NM8) have higher hardness than the one found in the normal cement mortar (CM0).

4.1.6. Ultrasonic pulse velocity (UPV) test:
As for the results gained from observing the Ultrasonic pulse velocity related to the quantities CM0 and MN mixtures, they are shown in figure (6). As found in compressive strength of the samples, ultrasonic pulse velocity increases by adding nano-ZrO\textsubscript{2} particles up to 1.25\% replacement (NM5). This velocity then decreases, despite the fact that the results of 2.0\% replacement (NM8) have higher velocity than the one of the normal cement mortar (CM0).
Figure 6. ZrO$_2$ content (%) and UPV test (Km/sec.) relationship.

4.1.7. Microstructure analysis (SEM):
Figure (7) (a-b) reflects an illustration to the microstructure analysis of specimens NM0, NM5. The specimens of the normal cement mortar have a crystal of Ca(OH)$_2$ of a great size as illustrated in figure (7-a) specially in the microstructure of cement mortar which lacks density and where empty spaces can be seen. In figure (7-b), it can be noted that NM5 has the most desirable mechanical properties an increase is found in nano-particles area with a percent of 1.25%. Thus, there is a complete improvement in the microstructure having effective density. This is because ZrO$_2$ affects the material in which the strength of the cement mortar develops and that causes an increase in compressive strength.

Figure 7 (a-b). The microstructure of the samples without and with ZrO$_2$ particles.

5. Conclusion:
The results of the experimental work for compressive strength and flexural strength it is found that ZrO$_2$ nano-particles addition up to 1.25% by the weight of cement could strengthen the cement by acting as filler. The voids of C-S-H gel structure are filled due to the reduction in the quantity and the size of Ca(OH)$_2$ calcium hydroxide crystals and lastly the structure of hydrated product is denser and compacted. The increasing of nano-particles quantity up to 2.0% there is decrease in the nano-particles distance and calcium hydroxide Ca(OH)$_2$ crystals because of the limited space which prevent the particles to grow to appropriate size. The agglomeration of ZrO$_2$ nano-particles causes the mechanical properties of the (NM8) mixture is close to the mechanical properties of ordinary cement mortar (CM0).

References

[1] Zhang, M., Li, H., (2011), "Pore structure and chloride permeability of concrete containing nano particles for pavement", Construction and Building Material, Vol.25, PP.608–616.

[2] Nazari, A., Riahi, S. (2011), "The effects of zinc dioxide nano-particles on flexural strength of self-compacting concrete", Composites: Part B 42, PP.167–175.

[3] Nochaiya, T., Chaipanich, A. (2011), “Behavior of multi-walled carbon nano tubes on the porosity and microstructure of cement-based materials”, Applied Surface Science, Vol.257 No.6, PP.1941–1945.

[4] Metaxa, Z., Seo, J., Konsta, M., Hersam, M., and Shah, S., (2012), “Highly concentrated carbon nano-tube admixture for nano-fiber reinforced cementitious materials”, Cement and Concrete Composites Vol.34, PP.612–617.

[5] Umar, Aj., Vahini, M., (2017), "Study of mechanical properties of concrete with nano zirconia”, international research journal of engineering and technology, vol. 04, PP.90–94.

[6] NANOSHEL-INTELLIGEN MATERIALS PVT. LTD, 2016, "Specification sheet", USA.

[7] Central Organization for Standardization and Quality Control, (1984), "Ordinary Portland cement" Iraqi standard No. (5)

[8] Central Organization for Standardization and Quality Control, (1984), "Aggregates and natural resources used in concrete and construction" Iraqi standard No. (45)

[9] Degussa, Construction Chemical "Glenium 51 technical data sheet" 06/97 MBT-ME revised 06/2008.

[10] ASTM C 305-12, (2012), “Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency”, ASTM, international, west Conshohocken, PA.

[11] Collins, F., Lambert, J., and Duan, W.H., (2012), “The influence of admixtures on the dispersion, workability, and strength of carbon nano-tube-OPC paste mixtures”, Cement& Concrete Composites, Vol.34, PP.201-207.

[12] Bui DD, Hu, J., and Stroeven, P., (2005), “Particle size effect on the strength of rice husk ash blended gap-graded Portland cement concrete”, Cement & Concrete Composites, Vol.27, No.3, PP.357–366.

[13] ASTM C109/ C 109M-02, (2002), "Standard Test Method for Compressive Strength of Hydraulic Cement mortars (Using 2-in. or [50-mm] Cube Specimens)”, ASTM, international, west Conshohocken, PA.

[14] ASTM C293-02, (2002), “Standard Test Method for Flexural Strength of Concrete (Using Simple Beam with Center-Point Loading)”, ASTM, international, west Conshohocken, PA.

[15] ASTM C642, (2001), “Standard Test Method for Density, Absorption, and voids in hardened concrete”, ASTM, Philadelphia, PA.

[16] ASTM D2240, (2015), "Standard test method for rubber property-Durometer hardness", ASTM international, west Conshohocken, PA.
[17] ASTM C597-02, (2002), "Standard test method for pulse velocity through concrete", ASTM international, west Conshohocken, PA.