The Effect of Nanomaterials on the Properties of Limestone Dust Green Concrete

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Abstract—Portland cement is considered the most involved product in environmental pollution. It is responsible for about 10% of global CO₂ emissions [1]. Limestone dust is a by-product of limestone plants and it is produced in thousands of tons annually as waste material. To fulfill sustainability requirements, concrete production is recommended to reduce Portland cement usage with the use of alternative or waste materials. The production of sustainable high strength concrete by using nanomaterials is one of the aims of this study. Limestone dust was obtained from a limestone quarry in Karbala. It was finely ground in the form of dust, most of it limestone, with CaCO₃ (Fe₂O₃), and sulphate (SO₃), are the principal components of limestone, with CaCO₃ and MgCO₃ being its major components [18]. Cements are primarily created by calcining a mixture of about 75% limestone and 25% clay to produce a calcium silicate clinker, which is then crushed and combined with a tiny amount of gypsum [19]. Nanomaterials are important due to properties such as the high surface to volume ratio. As the surface area per mass of a material increases, a larger amount of the material can come to contact with neighboring particles, therefore nanomaterials have high reactivity [20]. The inclusion of ultrafine nanomaterial particles fills the holes in the concrete microstructure. The nanopowder increases the surface area of the pozzolanic reaction, resulting in a more cementitious product [21, 22]. In the present research, the effects of nano-oxide (alumina) and limestone dust on concrete microstructure and mechanical properties are investigated.

Keywords—green concrete; limestone dust; nano Al₂O₃

I. INTRODUCTION

Concrete is a widely used construction material, with an annual production that exceeds 10 billion tons [2]. Durability, fire resistance, water impermeability, cost efficiency, energy efficiency, and the ability to produce on-site are some of its advantages. However, cement manufacturing, which is the primary binder in concrete, necessitates a significant quantity of natural resources and energy. Approximately 1.5 tons of raw ingredients are required to produce one ton of cement [3]. The need to reduce CO₂ emissions makes the search for alternative binders necessary. The necessity for more economical and environmentally friendly cement materials expanded the interest in other materials which can be used as substitutes to partially replace Ordinary Portland Cement (OPC) [4-6]. The cost of natural resources is increasing constantly, leading to the search for alternatives, such as recycled materials, rice husk ash, sawdust ash, tile powder, wood waste ash, silica fume, fly ash, coal bottom ash, limestone dust, Porcelinite, etc. [7-12]. Also, OPC is related to several diseases [13-17]. Limestone is the most prevalent type of calcium carbonate, often used in cement production. Calcium carbonate (CaCO₃), magnesium carbonate (MgCO₃), silica (SiO₂), alumina (Al₂O₃), iron oxide (Fe₂O₃), and sulphate (SO₃), are the principal components of limestone, with CaCO₃ and MgCO₃ being its major components [18]. Cements are primarily created by calcining a mixture of about 75% limestone and 25% clay to produce a calcium silicate clinker, which is then crushed and combined with a tiny amount of gypsum [19]. Nanomaterials are important due to properties such as the high surface to volume ratio. As the surface area per mass of a material increases, a larger amount of the material can come to contact with neighboring particles, therefore nanomaterials have high reactivity [20]. The inclusion of ultrafine nanomaterial particles fills the holes in the concrete microstructure. The nanopowder increases the surface area of the pozzolanic reaction, resulting in a more cementitious product [21, 22]. In the present research, the effects of nano-oxide (alumina) and limestone dust on concrete microstructure and mechanical properties are investigated.

II. MATERIAL CHARACTERIZATION

OPC produced by the Tassloja Cement Factory, confirming to Iraqi Specification No.5/2019 was used in this research [23]. Natural fine sand zone 2 (Table I), which is within the limits of the Iraqi Specification No. 45/1984 [24], was used as fine aggregates. Coarse aggregates with size of 5-14mm were used to prepare concrete samples. The physical and chemical properties of fine and coarse aggregates are shown in Tables II and III respectively. All concrete samples were produced with the same water to cement ratio (w/c) of 0.3. The concrete ingredients were mixed using 1:1.4:1.8 mixing ratio for cement, fine aggregates, and coarse aggregates respectively according to the British method for concrete mix design. Limestone dust was obtained from a limestone quarry in Karbala. It was finely ground in the form of dust, most of it passing the No.100 sieve. The chemical composition of the dust is given in Table IV. It was used to partially replace cement in concrete. Three different percentages (12%, 16%, and 20%) by weight were used to replace cement.

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The nanomaterial Al$_2$O$_3$ shown in Figure 1 was used as the partial replacement of cement. It was purchased from Skyspring Nanomaterials Ltd and its physical analysis is shown in Table V. Three different percentages of 0.5, 1, and 1.5wt% of cement were used.

The experimental part consisted of 7 concrete mixes as shown in Table VI (the concrete ingredients were mixed using 1:1.4:1.8 mixing ratio for cement, fine aggregates, and coarse aggregates respectively, according to the British method for concrete mix design).

Specimens in the shape of cube, prism, and cylinder were prepared to test compressive strength, flexural strength, and splitting tensile strength respectively. The steel molds were cleaned and their internal surfaces were lubricated with oil to prevent adhesion with concrete after hardening. The molds were filled with concrete in layers, and each layer was compacted by a vibrating table according to ASTM C-192/C192M [25], which is sufficient to remove any entrapped air. After compaction, the specimens were leveled by hand troweling, then left for 24 hours. The specimens were then removed from the molds, and were cured in water until the time of test. All specimens were cured in laboratory environment conditions according to ACI 308R-01 [26].

The tests performed on hardened concrete were the slump test, the compressive strength test, the flexural strength test, the splitting tensile strength test, and the SEM test.

### A. Workability (Slump Test)

The workability of concrete mixes was measured directly after mixing, according to ASTM C143 [27]. The results are shown in Table VII.

### B. Compressive Strength Test

The compressive strength of the concrete mixes was determined according to British Standard BS 12390-3:2019 [28] on 100×100×100mm cubes. The cubes were tested as shown in Figure 2 at the age of 7, 28, and 90 days. The average
result of three tested cubes was taken for each mix. The compressive strength for each cube was calculated as shown in (1):

$$F_{cu} = \frac{P}{A} \quad (1)$$

where $F_{cu}$ is the compressive strength (MPa), $A$ the face area of the cube ($mm^2$), and $P$ the compressive load at failure (N). The results are shown in Table VIII.

### TABLE VII. SLUMP TEST RESULTS

| Mix symbol | Slump (mm) |
|------------|------------|
| MR         | 102        |
| ML1        | 116        |
| ML2        | 122        |
| ML3        | 125        |
| MN1        | 117        |
| MN2        | 111        |
| MN3        | 107        |

C. Flexural Strength Test

Flexural strength was determined according to ASTM C 293-07 [29] by the center point method. The prism specimens with dimensions of 100×100×400mm were simply supported with 300mm span and were tested at the age of 7 and 28 days. The average of three prisms was taken for each mix. Modulus of rupture was calculated with:

$$F_r = \frac{3PL}{2bd^2} \quad (2)$$

where $F_r$ is the flexural strength (MPa), $P$ the maximum applied load indicated by the test machine (N), $L$ the average length of the specimen (mm), $b$ the average width of the specimen (mm), and $d$ the average depth of the specimen (mm). The results are shown in Table VIII.

D. Splitting Tensile Strength Test

Concrete cylindrical specimens with dimensions of 150×300mm were used in this test to determine the splitting tensile strength according to ASTM C 496-04 [30] using a compressive machine. In this test method, a diametric compressive force is applied along the side of a concrete cylindrical specimen until tensile failure occurs. The steel plate of the compressive machine is used to distribute uniformly the load applied along the length of the cylinder. The cylinders were tested at the age of 7 and 28 days, and the average of three cylinders was taken as the final result. Splitting tensile strength was calculated by:

$$\tau = \frac{2P}{\pi LD} \quad (3)$$

where $\tau$ the splitting tensile strength (MPa), $P$ the maximum applied load (N), $L$ the length of the specimen (mm), and $D$ its diameter (mm). The results are shown in Table VIII.

![Fig. 2. Compressive strength test.](image)

![Fig. 3. Compressive strength for all concrete mixes at the age of 28 days.](image)

![Fig. 4. Flexural strength for ML2 and MN3 mixes at 7 and 28 days.](image)

![Fig. 5. Splitting tensile strength for ML2 and MN3 at 7 and 28 days.](image)

E. Dry Density

The specimens were tested according to the Iraqi Guide 274 [31]. The average result of three samples was calculated at 7,
28, and 90 days for each mix after picking the cubes out of the curing water and drying their surfaces with a cloth. Density ($\rho$) is the mass of a unit volume of hardened concrete expressed in kg/m$^3$. The density was calculated from the specimen mass with volume of 100×100×100 mm obtained after air dry by:

$$\rho = \frac{M}{V}$$  \hspace{1cm} (4)

where $\rho$ is the density(kg/m$^3$), $M$ the mass of specimen at the time of test (kg), and $V$ the volume of the specimen calculated from its dimensions (m$^3$). The results are shown in Table IX.

**TABLE VIII. SUMMARY OF COMPRESSIVE, FLEXURAL, AND TENSILE STRENGTH TEST RESULTS**

| Mix symbol | Compressive strength (MPa) | Flexural strength (MPa) | Splitting tensile strength (MPa) |
|------------|---------------------------|------------------------|-------------------------------|
| MR         | 43.8 56.6 68.5            | - - -                  | - - -                        |
| ML1        | 40.6 53.3 66.0            | - - -                  | - - -                        |
| ML2        | 39.1 51.3 63.6            | 6.2 8.6 3.5            | 5.4                           |
| ML3        | 34.2 44.7 60.1            | - - -                  | - - -                        |
| MN1        | 40.4 51.8 64.9            | - - -                  | - - -                        |
| MN2        | 44.0 53.2 65.8            | 6.3 8.1 4.5            | 5.4                           |
| MN3        | 46.1 55.5 69.0            | 8.3 11.8 4.9           | 6.1                           |

**TABLE IX. DRY DENSITY RESULTS**

| Mix symbol | Dry density(kg/m$^3$) |
|------------|------------------------|
| MR         | 2511 2525 2536         |
| ML1        | 2452 2476 2481         |
| ML2        | 2437 2459 2470         |
| ML3        | 2523 2534 2541         |
| MN1        | 2540 2548 2557         |
| MN2        | 2556 2569 2580         |
| MN3        | 2556 2569 2580         |

| Mix symbol | 7 days 28 days 90 days |
|------------|------------------------|
| MR         | 2511 2525 2536         |
| ML1        | 2452 2476 2481         |
| ML2        | 2437 2459 2470         |
| ML3        | 2523 2534 2541         |
| MN1        | 2540 2548 2557         |
| MN2        | 2556 2569 2580         |
| MN3        | 2556 2569 2580         |

**F. Scanning Electron Microscopy (SEM)**

SEM was used to observe the products of nanomaterials. Figures 6 and 7 show the SEM results of a sample from the MLN concrete mix. For this observation, samples were taken from the cracked surface of the specimens of the concrete mixes. In Figures 6, 7 the samples prepared with nano Al$$_2$$O$$_3$$ show more density at C-S-H gel.

**G. Result Summary**

When adding limestone dust to the green concrete production, there was an improvement in workability and a slight decrease in the mechanical properties of concrete, but after adding nanomaterials, the properties began to increase again, so green concrete containing waste material with high properties can be produced. The importance of this research lies in the possibility of replacing a good percentage of cement with waste material while maintaining the same properties. The results of this study are similar with the findings in [21, 32].

**VI. CONCLUSIONS**

Based on the results obtained from the experimental investigation, the following conclusions can be drawn:

- Within certain ranges of strength and workability criteria, finely ground limestone dust can be recommended as a partial alternative for cement to produce green concrete.
- The dry density of concrete with limestone dust is always lower than that of normal concrete made with OPC only. When adding nano Al$$_2$$O$$_3$$, the dry density increases with the increase in nano Al$$_2$$O$$_3$$.
- From all the tested mixes, 16% dust by weight was found to be most satisfactory as it exhibits optimum compressive, tensile, and flexural strength, and a remarkable increase in workability.

**Fig. 6.** SEM image of concrete hydrated for 28 days with 1.5% nano-alumina.

**Fig. 7.** SEM image of concrete hydrated for 28 days with 1.5% nano-alumina with different scale.
This observation indicates that nano alumina has a good filler effect and further distribution of the particles in the remaining voids lead to a more homogeneous concrete matrix which increases the compressive strength of the produced concrete.

- Homogeneity was found to be increased with nano particle addition. This was due to the smaller size of the particles leading to an improvement in the surface characteristics of concrete by smoothening the grain and closing the pores thus increasing concrete strength.

- The addition of nano-alumina with limestone dust to the concrete mixture improved concrete properties and allows the production of high strength green concrete.

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