

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 in 12, 16, and 20% by weight of cement replaced cement in this study. The study was divided into two parts: the first was devoted to the investigation of the best percentage of replacement of waste lime. The second part of the study evaluated the performance of concrete when adding nanomaterials. Three percentages of cement replacement 0.5%, 1%, and 1.5% with nano-Al₂O₃ were used. The most efficient content of hydrated lime used in this study which achieves sustainability and maintains the quality of concrete was (16%). On the other hand, it was found that the best percentage of nano-Al₂O₃ as a partial replacement of cement is 1.5%.

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, conforming 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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TABLE I. NATURAL FINE SAND GRADING

Sieve size (mm)	Accumulative passing (%)	Accumulative passing (%) according to the limits of I.Q.S No.45/1984
10	100	100
4.75	100	90-100
2.36	88.7	75-100
1.18	66.9	55-90
0.6	51.8	35-59
0.3	18.8	8-30
0.15	3.4	0-10

TABLE II. PHYSICAL AND CHEMICAL PROPERTIES OF FINE AGGREGATES

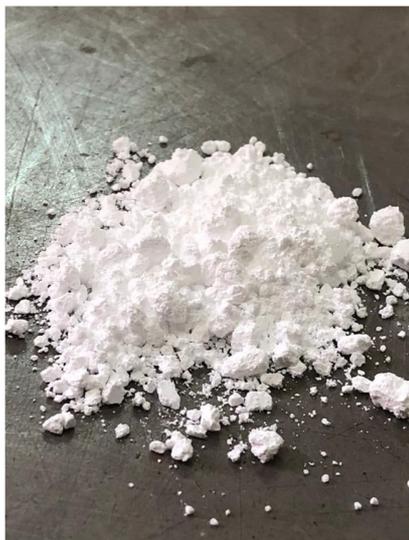
Properties of sand	Test results of sand	Limits of IQS No. 45/1984
Fineness modulus	2.76	-
Specific gravity	2.63	-
Absorption	0.8%	-
SO ₃	0.23%	≤ 0.5%
Dry rodded density	1604kg/m ³	-

TABLE III. PHYSICAL AND CHEMICAL PROPERTIES OF COARSE AGGREGATES

Properties of gravel	Test results of gravel	Limits of IQS No. 45/1984
Specific gravity	2.652	-
Absorption	0.7%	-
SO ₃	0.05%	≤ 0.1%
Dry rodded density	1640kg/m ³	-

TABLE IV. CHEMICAL ANALYSIS OF LIMESTONE DUST

Chemical composition	Constituent %
Silicon dioxide (SiO ₂)	5.15
Calcium oxide (CAO)	52.1
Aluminium oxide (Al ₂ O ₃)	0.66
Ferric oxide (Fe ₂ O ₃)	0.08
Magnesium oxide (MgO)	0.51
Sulphur oxide (SO ₃)	0.0
Loss on ignition	41.49

Fig. 1. Nano Al₂O₃ used in the research.

The nanomaterial Al₂O₃ 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.

TABLE V. PHYSICAL PROPERTIES OF NANO Al₂O₃

Property	Specifications
Appearance	Milky white
Crystal structure and type	Alpha
Purity %	99
Form	Powder
Density	3.5-3.9g/cm ³

III. EXPERIMENTAL PROGRAM

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).

TABLE VI. MIX DESIGN DETAILS FOR CONCRETE MIXES

Mix symbol	w/b	HRWRA (lt/100kg cement)	Cement (kg/m ³)	Limestone dust (kg/m ³)	Nano Al ₂ O ₃ (%)
MR	0.3	2.5	500	0	0
ML1			440	60	0
ML2			420	80	0
ML3			400	100	0
MN1			417.9	80	0.5
MN2			415.8	80	1
MN3			413.7	80	1.5

IV. SPECIMEN PREPARATION

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].

V. RESULTS

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):

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

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



Fig. 2. Compressive strength test.

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 $100 \times 100 \times 400 \text{mm}$ 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:

$$F_r = 3PL/2bd^2 \quad (2)$$

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 $150 \times 300 \text{mm}$ 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:

$$\tau = 2P / \pi LD \quad (3)$$

where τ 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.

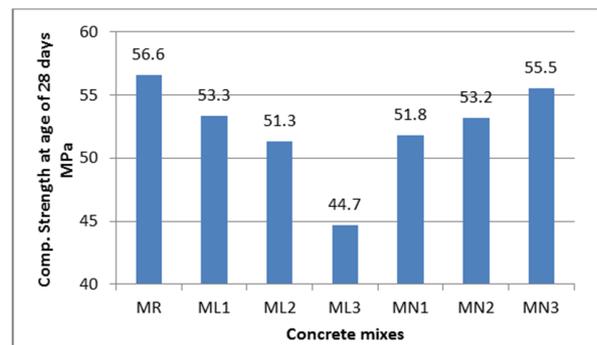


Fig. 3. Compressive strength for all concrete mixes at the age of 28 days.

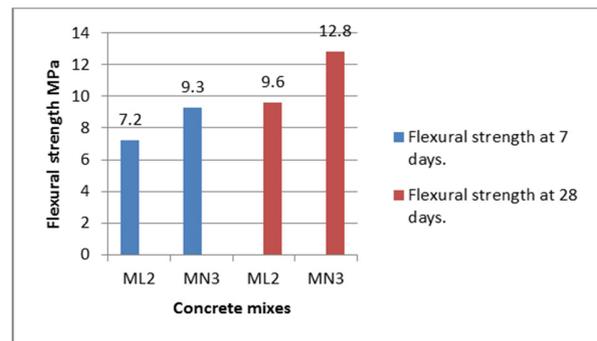


Fig. 4. Flexural strength for ML2 and MN3 mixes at 7 and 28 days.

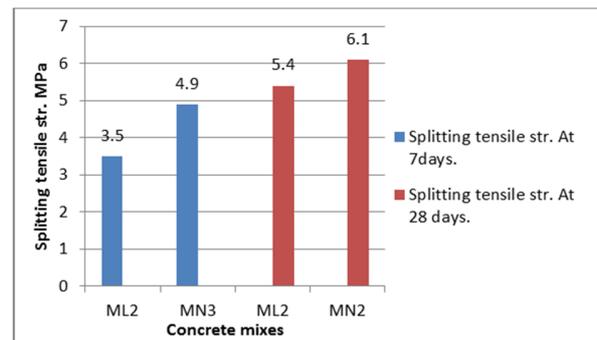


Fig. 5. Splitting tensile strength for ML2 and MN3 at 7 and 28 days.

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 (ρ) 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 $100 \times 100 \times 100$ mm obtained after air dry by:

$$\rho = M / V \quad (4)$$

where ρ 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)	
	7 days	28 days	90 days	7 days	28 days	7 days	28 days
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	-	-	-	-
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)		
	7 days	28 days	90 days
MR	2511	2525	2536
ML1	2452	2476	2484
ML2	2449	2472	2481
ML3	2437	2459	2470
MN1	2523	2534	2541
MN2	2540	2548	2557
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_2O_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_2O_3 , the dry density increases with the increase in nano Al_2O_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.

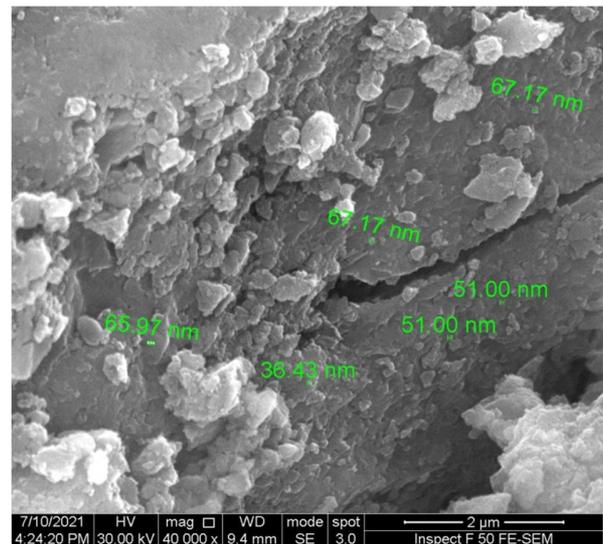


Fig. 6. SEM image of concrete hydrated for 28 days with 1.5% nano-alumina.

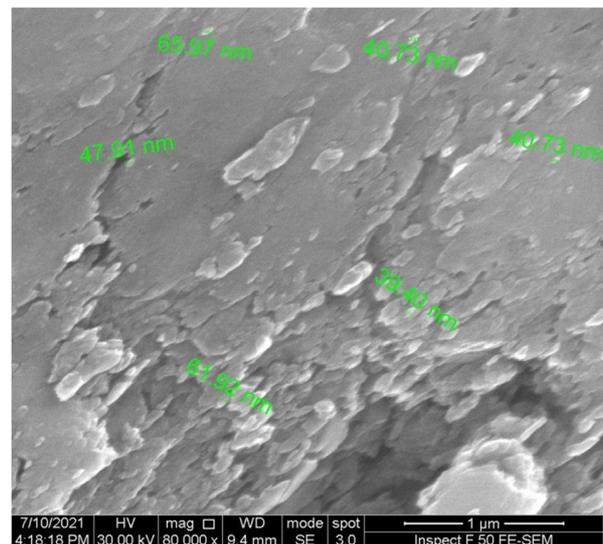


Fig. 7. SEM image of concrete hydrated for 28 days with 1.5% nano-alumina with different scale.

- The compressive strength result of samples with nano alumina showed that the combination of nano-particles and micro-particles of limestone dust increased the compressive strength of concrete samples compared with the compressive strength of concrete with only limestone dust.

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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