Effect of Nano Calcium Carbonate on Some Properties of Reactive Powder Concrete

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Abstract. Concrete is the most commonly used construction material, and its use is expected to rise as the world's population grows, the economy develops, and aging infrastructure needs to be repaired or replaced. Unfortunately, one of its main constituents, cement, is responsible for approximately 5–10% of global carbon dioxide emissions. As a result, the industry as a whole and the specific material are in desperate need of re-evaluation. In this research, the effects of Nano calcium carbonate (NC) on some properties of reactive powder concrete (RPC) were studied. Nano calcium carbonate (NC) was added at rates (0.75, 1, and 1.5)%. As a partial replacement of cement weight, Reactive powder concrete (RPC) was developed from cement, nano CaCO₃, recycled fly ash, silica fume, fine sand, steel fibers, superplasticizer, and water. Compressive strength tests, tensile strength tests, flexural strength were conducted at 7 and 28 days. Water absorption was specified at the age of 28 days. The results showed the addition of NC to the RPC improved the mechanical properties compared with the mixture without NC. Also, the incorporating of nano-CaCO₃ in RPC will contribute in produced RPC more environmentally friendly by reducing its cement factor, While achieving good engineering properties.

Keywords: Construction material; Nano calcium carbonate; reactive powder concrete; cement; fly ash; silica fume.

1. Introduction

Nanotechnology focuses on producing new materials at the molecular level with dramatically improved mechanical and related properties. Material behavior concerns can be solved by nanoscale engineering techniques with the thorough application of nanotechnology techniques. This allows for a deeper understanding of the molecular properties of materials and the creation of new materials [1]. The four main effects of nanoparticles, including size effect, quantum effect, surface effect, and interface effect, have piqued people's interest. The efficiency and properties of materials could be improved by incorporating nanoparticles into cement. A nanoparticle is a cluster of tens to thousands of atoms with a 1–100 nm diameter that can be used as a simple nanotechnological building block. When nanoparticles are made from the ground up, the particle size and shape can be influenced by manufacturing conditions. These particles may also be known as nanocrystals because the atoms within them are perfectly arranged. As the size of the fabric is reduced from macro- to nanoscale, significant variations in conductivity, optical absorption, chemical reactivity, and mechanical properties emerge [2]. Nano CaCO₃ is commonly used in cementitious composites because of the physical and chemical impact on their properties, such as the filler effect and nucleation effect. However, the agglomeration of nano CaCO₃ will significantly reduce its effects [3].

Nanoparticle incorporation in concrete provides various benefits, including ultra-high compressive strength, high break tensile strength and ductility, high aggregate paste bonding, and improved thermal
resilience – making it ideal for use in refractory concrete [4]. Some studies on integrating nanoparticles of calcium carbonate into the cementitious materials have been released. Shaikh and Steve [5] studied the effect of incorporating nanoCaCO$_3$. In different proportions, 1 and 4% were added to concrete with a high content of Fly ash (40 and 60%) as a partial substitute for cement weight. This study found that 1% of NC worked to improve the resistance and durability properties of concrete. In another study, Sun et al. [6] reported Calcium CarbonateNanoparticles and Fly Ash's effects on the strength and permeability of concrete, and the consequences display the samples containing nano CaCO$_3$ best development in mechanical properties. Increased concrete energy is made from the nanoparticles' chemical response with the factors in the concrete.

Long et al. [7] evaluated the change in fresh concrete behavior by conducting workability, setting time, and calorimeter tests of concrete containing high volume fly ash HVFA with nano CaCO$_3$. In that experiment, the ordinary Portland cement was replaced with class C Fly Ash 35% and 45%. Nano CaCO$_3$ was added in proportions of 1 and 3% of the weight of the cement. They found that the addition of nanoparticles will accelerate the rehydration reactions and improve the early strength. On the other hand, it was concluded that these particles' addition leads to a decrease in the modulus of elasticity and the hydration heat.

2. Experimental work

2.1 Cement

The ordinary Portland cement (OPC) used in this study It within the Iraqi Specification IQS No. 5/2019 type / (42.5 N) [8]. The chemical composition of cement is shown in Table 1.

| Compound composition | Result | limit of Iraq specification No. 5-2019 |
|----------------------|--------|----------------------------------------|
| CaO                  | 62     | --                                     |
| SiO$_2$              | 22     | --                                     |
| Al$_2$O$_3$          | 5.3    | --                                     |
| Fe$_2$O$_3$          | 3.4    | --                                     |
| SO$_3$               | 2.2    | Max 5                                  |
| MgO                  | 2.1    | Max 2.8                                |
| I.R                  | 0.9    | Max 1.5                                |
| L.O.I                | 2.5    | Max 4                                  |

2.2 Fine aggregate

AL-Ukhaider Natural sand as a fine aggregate used in concrete mixes of this work. The chemical and physical properties of the sand are within the limit specified by Iraqi standard, zone /4. IQS No.45/1984 [9].

2.3 Mixing water

The water used in this research within Iraqi to spes.No.1703/1992 [10].

2.4 Silica fume (SF)

Micro silica from Company (CONMIX) used in this work. The percentages used were 10%, replacement with cement weight. SF used in this work within the requirements of ASTM C1240-15 [11].

2.5 Fly ash (FA)

According to the standard to American Standard (ASTM C 618-15) [12]. In this research, the fly ash class (F) (8) % proportion was used to replace cement weight.
2.6 Micro steel fibers (MSF)
The (MSF) used in this test program was straight steel fibers manufactured in China. The diameter of fiber used 0.2 mm and the length 13 mm so (L/d = 65). Fibers were added as 1% of the concrete volume.

2.7 Nano calcium carbonate (NC)
The nano calcium carbonate or nano CaCO$_3$ used in this study are nanoparticles imported from Skyspring Nanomaterial. It was of a high degree of purity, and the well-defined diameter range of the particle size is less than (100) nm. It contained more than 97.5% of CaCO$_3$ and in powder form. The use of it as replacing with cement.

2.8 Superplasticizer (SP)
Master Glenium 51 (SP) according to ASTM C494 [13] used in this research. The manufacturer's recommended dosage was in the range (0.5-1.6) liters/100 kg of the cement. 1 liter/100 kg cement the dosage is using in this study.

2.9 Concrete mixes
The mixtures were prepared in this work using experimental mixtures based on specifications and guidelines presented in the previous research. The batches were prepared as a trial to obtain a compressive design strength of 90 MPa, which is the reference mixture for comparison with other mixtures. A total number of four Reactive powder concrete (RPC) mixtures prepared by using water to binder ratio about (0.275), The content of the binder used in this research 800 kg/m$^3$, HRWR(Glenium 51) used 8 Liters by weight of cement. The experiment program included made the control mix with only Portland cement in addition to silica fume and Fly Ash (PC+SF+FA) as the binder, while other mixtures included replacing the cement with nano calcium carbonate (NC) (PC+NC +SF+FA) in which a percentage of PC was replaced with nano calcium carbonate (NC) at 0.75%, 1% and 1.5% by mass of total cementitious materials. Mix proportions details for RPC are shown in Table 2.

| Mix. No. | Details | OPC (kg/m$^3$) | SF (kg/m$^3$) | Fa (kg/m$^3$) | Nc (kg/m$^3$) | Fine Agg (kg/m$^3$) | Weight water (kg/m$^3$) | MSF 1% By vol. of concrete |
|----------|---------|----------------|--------------|--------------|--------------|---------------------|--------------------------|---------------------------|
| Mr       | 0%NC    | 656            | 80           | 64           | 0            | 880                 | 220                      | 1                         |
| M1       | 0.75%NC | 650            | 80           | 64           | 6            | 880                 | 220                      | 1                         |
| M2       | 1%NC    | 648            | 80           | 64           | 8            | 880                 | 220                      | 1                         |
| M3       | 1.5%NC  | 644            | 80           | 64           | 12           | 880                 | 220                      | 1                         |

3. Experimental tests

3.1 Compressive Strength Test
According to ASTM C109 [14], the compressive strength test is determined by using standard cube specimens of 50×50×50 mm. The Compressive strength ($f_m$) is calculated with the following equation.

$$f_m = \frac{P}{A}$$  \hspace{1cm} (1)

where
- $f_m$ = compressive strength in MPa
- $P$ = total maximum load in N
- $A$ = area of loaded surface in mm$^2$

3.2 Splitting tensile strength test
The tensile strength was determined in this study according to ASTM C 496 [15]. This test was performed using a standard cylinder model 100×200 mm. The splitting tensile strength (T) calculated according to the following equation:
\[ T = \frac{2P}{\pi L d} \]  
(2)

Where
- \( T \) = splitting tensile strength (MPa).
- \( P \) = max. applied load (N).
- \( L \) = the length of specimen (mm).
- \( D \) = diameter (mm).

### 3.3 Flexural Strength Test

In this study, the flexural strength test was determined according to ASTM C78 [16] by using prisms

Samples 50×50×300 mm in size, and the following equation calculated the flexural strength (R):

\[ R = \frac{PL}{bd^2} \]  
(3)

Where:
- \( R \) = modulus of rupture.
- \( P \) = maximum applied load indicated by the testing machine.
- \( L \) = span length.
- \( b \) = average width of the specimen at the point of fracture.
- \( d \) = average depth of specimen at the point of fracture.

### 3.4 Absorption test

The water absorption at the 28-day of the specimens was measured using ASTM C642-13 [17]. The water absorption ratio is calculated by averaging the results of three specimens using the equation below.

\[ \text{Absorption (\%)} = \frac{(B - A)}{A} \times 100 \]  
(4)

Where
- \( A \) = oven-dry weight (g).
- \( B \) = saturated surface dry weight (g).

### 4. Results and Discussion

#### 4.1 Compressive strength

The compressive strength changes for RPC at 7 and 28 days are clarified in Table 3 and Figure 1. The results showed all mixtures containing nano carbonate (NC) recorded a higher compressive strength than control. The increase in compressive strength compared to the control mixture was (11.4, 39.3, 23.7) % at 7 days, (5.8, 28.2, and 4.6) % at 28days also the results show 1% of NC exhibited the highest compressive strength at all ages (7 and 28) day, in comparison to other replacement contents. Increase the strength of concrete is due to the mechanism of action of nanoparticle calcium carbonate, where it can be explained as follows: when a small number of nanoparticles are uniformly dispersed, it will lead to the precipitation of cement hydrate products due to its high surface energy during the hydration process, so they grow and form a clump containing nanoparticles as a nucleus that works on increasing and accelerate the hydration process. This conclusion meets what previous researchers recorded [5,19].

According to the theory of Wu’s ‘centroplasm’ aggregate particles are considered as central particles that act as a body structure while the gel is a transporter material and the bonding force that creates between the central particles and the transport material significantly affects the strength of the concrete, so the nanoparticle act as nucleation sites, These nanoparticles accelerate cement hydration and increase the dissolution rate of C3S, and as a result the rapid formation of C-S-H in cement paste. On the other hand, the nanoparticles that diffuse between the products of rehydration will inhibit the formation of Ca (OH)2 and AFM which reduces the strength of the concrete, also, fills the pores around the cement particles, causing a decrease in permeability and thus an increase in early strength [1].
Table. 3. Compressive strength value.

| Max. No. | (NC) % | Compressive strength (MPa)   |
|----------|--------|-------------------------------|
|          |        | 7 day                         |
|          |        | 28 day                        |
| MR       | 0      | 73.78                         |
| M1       | 0.75%  | 82.2                          |
| M2       | 1%     | 102.82                        |
| M3       | 1.5%   | 91.3                          |

Afterward, this increased value decreases slightly when 1.5% of NC is included because the increase of NC addition leads to not being well distributed the hydration products evenly, and thus it will create a weak zone causing a decrease in concrete strength. In addition to that in the wet mix as its higher van der Waal’s forces are higher than cement, increase viscosity, reduced flowability, increase of the voids and permeability Consequently, hence Decreased the strength of the concrete, when NC increased, But the strength remained higher that of control RPC (0% NC). RPC mixture which contains 1% NC has been chosen as the optimal percentage of nano- CaCO_3 content., where mix 1% NC showed (102.28) and (117.96) MPa at the curing age of 7, 28 days, respectively, while the control mix exhibited a compressive strength of (73.78) and (91.95) MPa for age 7, 28 days, respectively. This is consistent with findings of reference [20].

Figure 1. relationship between Nano carbonate( NC) percentage and compressive strength of RPC.

4.2 Splitting tensile strength test
The splitting tensile strength results for 7 and 28 days of RPC mixtures containing CaCO_3 nanoparticles (NC) and control mixture without (NC) obtained in this study are presented in Table 4 and Figure 2.

Table 4. Splitting tensile strength of RPC mixtures.

| Max. No. | NC % | Splitting strength (MPa) |
|----------|------|--------------------------|
|          |      | 7 day                    |
|          |      | 28 day                   |
| MR       | 0    | 6.17                     |
| M2       | 1    | 6.89                     |
|          |      | 7.215                    |
|          |      | 9.38                     |
The addition of fine particles will strengthen the concrete material and block many of the pores. This conclusion was proven by ([21]. The current study's conclusion shown splitting the tensile strength of RPC with (NC) is greater than the control mix, about 11.6% at 7 days and 30% at 28 days. This increase due to the nanoparticles' small size will fill the voids in the CHS structure, thus producing denser concrete. This is also similar to the results that (Dawood and Abdullah, 2020)[22] founded. Also, the increase in the number of nanoparticles in the cement will increase the proportion of the formed C-S-H gel and increase bond strength with the concrete components. Thus, the tensile strength will be improved. This conclusion was recorded by reference [23].

4.3 Flexural strength
In Table 5. and figure 3. The effect of nano calcium carbonate (NC) on flexural strength RPC is summarized. The results are evident the samples containing the nanoparticles of NC achieved the highest flexural strength compared to the control. Also, the samples' flexural strength containing 1% (NC) about 17.4% at 7 days and 11.7% at 28 days higher than the control sample. In general, the reason is due to consumption of (CH) by nano CaCO₃ through the hydration of cement. As a consequence, It causes many hydration products that lead to increased early strength of RPC. In addition to that, the nanoparticles lead to a denser microstructure. This is also in agreement with what has been achieved [7].

**Figure 2.** Relationship between Nano carbonate (NC) percentage and splitting tensile strength of RPC.

**Figure 3.** Relationship between Nano carbonate (NC) percentage and flexural strength of RPC.
Table 5. Flexural strength of RPC mixtures.

| Max. No. | NC % | Flexural strength (MPa) |
|----------|------|------------------------|
|          |      | 7 day                  | 28 day |
| MR       | 0    | 8.72                   | 10.24  |
| M2       | 1    | 10.24                  | 11.44  |

4.4 Total water absorption

In this study, the results in Table 6 and Figure 4 explain that RPC samples contain 0.75%, 1% and 1.5% NC at age 28 days less water absorption (WA) than the control mix. This is because adding nanoparticles into the concrete will increase the formation of hydration products that close the pores and reduce the permeability. These conclusions were also confirmed by [5]. The lowest reduction of WA was obtained from the RPC with 1% NC which provided 0.96%, while the control mix recorded 1.28% at 28 days. This corresponds to other studies [24,25].

Table 6. Result of total water absorption.

| Max. No. | NC (%) | Absorption% at 28 day |
|----------|--------|-----------------------|
| MR       | 0      | 1.28                  |
| M1       | 0.75   | 0.964                 |
| M2       | 1      | 0.96                  |
| M3       | 1.5    | 0.97                  |

Figure 4. Relationship between Nano carbonate (NC) addition and absorption of RPC.

5. Conclusions

The following conclusions were reached through the experimental results obtained from this research:

- The replacement of NC with cement led to the filling of the pores around the cement particles and its chemical effectiveness, which increased hydration products' formation. Also, the effect of hydration of the nanoparticles led to a decrease in the demand for the volume of water, thus reducing the permeability and improving the mechanical and durability properties of RPC.
- The compressive strength of reactive powder concrete (RPC) increasing with the replacement of the (NC) with cement. The mix with 1% (NC) replacement with cement had significantly
investigated higher compressive strength where it is recorded about 39.3% and 28.2 % more than control mix at ages 7 and 28 days, respectively.

- Inclusion of nanoparticles of calcium carbonate in concrete increases the splitting tensile strength, as the replacement ratio (1%) of NC improved up 11.6% and 30.8 of tensile strength more than reference mix, at the ages 7 and 28 days.
- The replacement (NC) with cement in the mixtures led to an increase in the flexural strength of RPC where 1% replacement of cement weight with NC could significantly investigate higher density values about 17.4% and 11.7% higher than reference mix at 7 and 28 days, respectively.
- The nanoparticles permeated into the concrete led to reducing the total water absorption values of about (24, 25, 24%) for using (0.75, 1, and 1.5%) NC compared with the control mix at age 28 days.
- A new type of RPC can be developed by using NC to improve the properties of strength and durability and work to reduce environmental pollution caused by carbon dioxide released from cement production plants and reduce the cost of concrete.

Acknowledgments
This work was carried out to achieve sustainable development by protecting the environment from pollution resulting from the Portland cement industry, represented by the release of CO₂ gas and the use of more environmentally friendly materials. Therefore, this work will serve the Ministry of Industry and Minerals and the Ministry of Environment, Housing, and Reconstruction.

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