Production of friendly cementations materials containing nano limestone powder

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ABSTRACT. Carbon dioxide gas emission from cement production is the result of the burning process and de-carbonation of limestone and cement material. Reducing carbon dioxide is a global challenge. The main objective of this study was to find an ideal alternative to cement in order to decrease energy consumption and carbon dioxide releases. Using limestone powder to replace cement binder is considered an effective method to reduce carbon dioxide emissions from cement production. This study focuses on the relationship between replacement levels of limestone powder for ordinary Portland cement and some properties of cement mortar. Using limestone powder as an admixture decreases compressive strength, thus the super-plasticizer content should be decreased in order to obtain the equivalent strength of plain cement. This research used nano-particle size limestone powder to replace with cement in a different ratio. The results showed that mortar cement containing a higher proportion of limestone powder reduces hydration temperature and reduces the compressive as well as flexural strength but it has also shown a significant increase in workability due to the effect of limestone powder. Because of the weakening effect that is related to the replacement of a part of cement, there is a drop in the mechanical properties of the cement mortar.

Keywords
Nano-Limestone Powder, Limestone Particle Size, Calcium Carbonate, Cement Substitute, Carbon Dioxide Gas Emission.

1. Introduction
Cement is one of the most used materials for construction purposes around the world. More than 10,000,000,000 tons per year is produced causing significant environmental and economic impacts [1]. In addition, it consumes a large quantity of Non-renewable raw materials, and energy during the period of production. For the purpose of producing less harmful concrete to the environment, a part of the cement used can be replaced by limestone powder or complementary cement materials (SCMs) such as silica fumes, fly ash, and ground granular blast furnace slag [2]. The reduction of cement content in concrete is one of the persistent global sustainability concerns of the 21st century [3]. Cement has the greatest footprints when it comes to CO2 release and energy consumption [3, 4]. One of the materials used in concrete in some parts of the world for many years, but it has renewed interest worldwide, is limestone powder, which is usually available in the form of Calcium polymers of
calcium carbonate and varying degrees of magnesium (carbonate) [5, 6]. Since limestone is the main source of calcium for cement production, as well as being one of the most widely used aggregates, its presence is everywhere in the concrete industry [7]. While commercially, high-purity limestone powders are produced for use in the cosmetic, food, paint, paper, pharmaceutical, polymeric and concrete industries (to name a few) [8], the purity is less but more economic materials are obtained as dust can provide. The fracture resulting from the total crushing process, for example, has significant performance advantages in concrete [9]. On the other hand, the invention of nano-particle materials stimulated the researchers to conduct several studies on the inclusion of these materials in the concrete structure and their excellent positive effects on the mechanical properties. For example, previous experiences have shown that adding nano-particle silica (40 nm (1.57 lin)) improved the strength of the cement mortar at an early age by about twice than the result of the addition of small silica (SF) (0.1 lumens (3.94 lin)). The advantage of using nano-particle limestone powder compared to other nanoparticles materials is the availability of large quantities and reasonable costs [10].

2. Experimental Program
The aim of the research is to evaluate the effects of replacing a part of cement with nano-particle size limestone powder on some properties such as compressive strength, flexural strength, temperature and workability.

3. Mixture Proportions
In each proportion (10%, 20% and 30%) of Nano particle size limestone powder replacement, 9 specimens of 5 cubic cm were produced for compressive strength test, and 9 specimens of 4cm×4cm×16cm prisms were produced for flexural strength test. The mixes design is shown in Table1. Cement mortar was mixed and designed in according with ASTM C305-14 [14]. Immediately after mixing, fresh mixture has been tested to calculate its workability (flow table) and temperature. After 24 hours of casting, samples were removed from molds and curried with a humid atmosphere of 100% and temperature of 25°C until the testing process was complete.

| Ingredients type | Mix | Control | α   | β   | γ   |
|------------------|-----|---------|-----|-----|-----|
| Cement           | 250 g | 225 g   | 200 g | 175 g |
| Limestone powder | -   | 25 g    | 50 g  | 75 g  |
| Sand             | 687 g | 687 g   | 687 g | 687 g |
| Water            | 70 mL | 70 mL   | 70 mL | 70 mL |
| Super Plasticizer| 4 mL  | 4 mL    | 3.5 mL | 3 mL  |
| W/C              | 0.28  | 0.28    | 0.28  | 0.28  |

*Alpha – 10% replacement *Beta – 20% replacement *Gamma – 30% replacement

3.1 Materials used
In this research, Type I ordinary Portland cement meeting (ASTM C150, 2015) [11] was used then partially replaced with nano-particle size powder of limestone. The replacement ratios of limestone were 10%, 20%, and 30% of the weight of cement. The effective diameter of limestone powder particle is (184.5 nm) and the specific gravity is (2.78). The cement mortar mixture consisted of natural Sand of the river with the fineness modulus of (2.68) and the specific gravity equal to (2.61). W/c ratio was maintained at (0.28) in each mixes. The super plasticizer used was (fosroc structuro 520) [15] with dose (1.6, 1.4 and 1.2 liter) for each 100 kg of cement.

3.2 Limestone Powder Properties

In this research, Limestone stone was used from the western desert region of Iraq, specifically from the city of Samawa, and was ground by using a quick crusher with a speed of 25000 cycles per minute until reaching the desired milling level. The tests were then carried out for the purpose of finding the granular size of the limestone powder. The results showed that the effective diameter of the particles is 184.5 nm as shown in Figure 1.

![Figure 1 Limestone particle size](image)

4. Results and discussions:

4.1 Fresh Mix Properties:

4.1.1 Mix Temperature. This test was conducted according to ASTM C1064M [16]. The properties of fresh mixture with nano-particle size limestone powder are important due to the relationship between it and the hydration of cement mortar. Table (2) shows the test results for mixture
temperature, ranging from \((24.5 \, ^\circ C \) to \(25.9 \, ^\circ C\)). The mix temperature decreased gradually with higher amounts of nano-particle size limestone powder in the batch. The slight reduction in temperatures with different mix designs proves that no reaction occurred between cement and nano-particle size limestone powder, and this slight change occurred due to the decrease in cement content.

**Table 2** The effect of limestone powder on mix temperature.

| Mix design | Temperature (°C) |
|------------|------------------|
| control    | 25.9             |
| α          | 25.2             |
| β          | 24.6             |
| γ          | 24.5             |

*Alpha – 10% replacement *Beta – 20% replacement *Gamma – 30% replacement

**4.1.2. Workability.** This test was conducted according to ASTM C230 / C230M -14, where the value of the mixer workability can be controlled according to the type of work required [17]. The flowability of the newly poured batch was calculated by conducting a flow table test. The test results of the flow table are presented in Table 3. The flow table or workability increased slightly in spite of reducing the dose of superplasticizer due to limestone powder presence in mixture, and most importantly at 30% substitution levels. Because the limestone powder absorbs less water than cement, the amount of free water in the mixture is higher than the reference mix, which will cause increase in workability; the greater percentage of replacement will cause a greater increase in workability.

**Table 3** Workability of fresh cement mortar.

| Mix Design | Workability (flow table) |
|------------|--------------------------|
| control    | 18cm                     |
| α          | 18.2cm                   |
| β          | 18.5cm                   |
| γ          | 18.8cm                   |

*Alpha – 10% replacement *Beta – 20% replacement *Gamma – 30% replacement

**4.2. Hardened Mix Properties**

4.2.1. Compressive Strength. The compressive strength of cement mortar was tested using the compression-testing machine in accordance with ASTM C109 / C109M [12]. In general, the compressive strength is usually considered as a very important characteristic (especially when nano-particle limestone powder is used to replace a part of cement due to the negative effects on strength). It also generally gives an indication for the quality of cement mortar and cement paste structure. Table 4 shows the calculated average of compressive strength from 3 samples in 7 days, 28 days and 56 days. In addition, Figure 2 shows the results of compressive strength test for cement mortar replacing 10%, 20% and 30% of the nano-particle limestone powder and compared it with control mix which does not contain any additives. The replacement of the limestone adversely affected the compressive strength due to the decrease in the main bonding material (cement), where it became clear from the experiments that the limestone powder is chemically inactive and does not contribute to chemical reactions even during long ages.
Table 4 Average of compressive strength with different limestone powder proportion.

| Mix type (MPa) | 7 Days | 28 Days | 56 Days |
|----------------|--------|---------|---------|
| control        | 26.5   | 31.8    | 33.2    |
| α              | 25.6   | 31.2    | 32.7    |
| β              | 23.8   | 29.3    | 31.1    |
| γ              | 22.1   | 26.9    | 28      |

*Alpha – 10% replacement *Beta – 20% replacement *Gamma – 30% replacement

Figure 2 Influence of cement replacement with Nano-particle size limestone powder on compressive strength

4. 2. 2. Flexure Strength. The flexure strength of cement mortar was conducted using the (3-point loading test method) in accordance with (ASTM C348-18) [13]. Table 3 shows the flexure strength of three samples tested for flexure strength failure. Figure 3 shows how the size and level of different particles of limestone ground powder in batch affects the bending strength of the cement mortar. The limestone replacement with cement negatively affects the flexure strength. The result shows that the cement replacement by 10% limestone reduces the flexure strength by 3% to 5%, and the cement replacement by 20% limestone reduces the flexure strength by 5% to 15%, whereas a 30% cement replacement by limestone decreases the flexure strength by 8% to 26% as in the case of compression strength.
Table 5 Flexural strength with different limestone powder proportion.

| Mix type (MPa) | 7 Days | 28 Days | 56 Days |
|---------------|--------|---------|---------|
| control       | 10.35  | 12.82   | 14.07   |
| α             | 9.87   | 12.33   | 13.52   |
| β             | 8.68   | 12.46   | 13.4    |
| γ             | 7.61   | 12.06   | 12.97   |

*Alpha – 10% replacement *Beta – 20% replacement *Gamma – 30% replacement

Figure 3 Influence of cement replacement with Nano-particle size limestone powder on flexural strength diagram

4.3. CO₂ emission:
According to the percentages of substitution used in this research and based on previous studies and researches [18], it is clear to us that the replacement of part of the cement with limestone has a significant impact on the emission of carbon dioxide, which is caused by the basic process of the cement industry. Where the ratio of replacement of 10% led to a decrease in the emission of carbon dioxide by (-7.81%), 20% led to a decrease in the emission of carbon dioxide (-15.62%), and finally the replacement rate of 30% led to a decline in emissions by (-23.43%) as shown in Table 6.
Table 6 CO₂ emission with different ratios of cement replacement.

|                      | CO₂e kg/m³ | control | α         | β         | γ         |
|----------------------|------------|---------|-----------|-----------|-----------|
| cement               |            | 607.5   | 546.75    | 486       | 425.25    |
| Limestone powder     | ---        |         | 7.5       | 15        | 22.5      |
| Water                | 0.3        | 0.3     | 0.3       | 0.3       |
| River sand           | 5.5        | 5.5     | 5.5       | 5.5       |
| Transportation       |            | 29.6    | 29.6      | 29.6      | 29.6      |
| production           | 38.9       | 38.9    | 38.9      | 38.9      |
| Total CO₂e kg/m³     |            | 681.8   | 628.55    | 575.3     | 522.05    |
| CO₂e Reductions      | 0.0%       | 7.81%   | 15.62%    | 23.43%    |

*Alpha – 10% replacement *Beta – 20% replacement *Gamma – 30% replacement

5. Conclusion
This study examined the effect of replacing high percentages of cement with limestone powder on the properties of cement mortar when the limestone powder was added to the mixture during the mixing process. The experiments proved that the inclusion of limestone powder in the mixture as an alternative to a part of the cement at high volume has positive effects on both the environment and some properties of cement mortar. The concentration of limestone powder at high rates is more effective in the aspect of reducing the emission of carbon dioxide, as well as some mechanical properties such as workability and temperature of fresh cement mortar. The use of limestone powder with Nano-particle size as an alternative to cement negatively affects the compressive strength and flexural strength of the cement mortar because it is a chemically inert substance and does not react with cement even at later ages. The effect of cement replacement with Nano-particle size limestone powder on the mechanical properties of fresh cement paste is more pronounced when the percentage of substitution is increased, a slightly decrease in the temperature of the mixture was observed at 10% replacement. This decrease in temperature was gradually increased as the percentage of substitution increased, while the experiments showed an increase in workability directly proportional to the increase in replacement ratio. The cement replacement with Nano-particle size limestone powder will cause a reduction in CO2 emissions; this reduction is directly related to the replacement level. The loss of strength when replacing a low level is greater than the benefit of reducing emissions but when replacing cement at higher levels, the benefits of reducing emission outweighs the compressive strength loss.

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