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Investigation of Strength and Cracking Behaviour of $ZnCo_2O_4$ Nanoparticles Incorporated Porous Concrete

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ABSTRACT

In this study, the effect of limewater on strength assessments and percentage of water absorption of zinc cobaltate ($ZnCo_2O_4$) nanoparticles incorporated porous concrete has been investigated. Portland cement was partially replaced by $ZnCo_2O_4$ nanoparticles with the average particle size of 50 nm. The results indicated that the incorporation of nanoparticles could transform concrete with improved strength and water permeability when the specimens are cured in saturated water. The strength of concrete specimens without nanoparticles are relatively low compared to the specimen with $ZnCo_2O_4$ nanoparticles. The results show that the strengthening of nanoparticles incorporated specimens resulted from improved permeability together with high strength. Microstructure and morphology of the specimen after compressing test was observed by scanning electron microscopy (SEM). In addition, $ZnCo_2O_4$ nanoparticles are able to act as nanofillers and recovered the pore structure of the specimens by decreasing damaging pores.

1. Introduction

The quality and admixture control are one of the major problems of the concrete pavement, which is typically used for road surfaces, heavy load container, bridge decks, airfield runways and parking lots [1]. It is important to characterize the discharge from all sites, so that pollution control plans may be developed. Porous concrete is a highly practiced type of nanomaterials, which has great performance and appropriate strength. It can also form with less aggregate and water-controlled pieces [1, 2]. Consequently, the types of cementations materials, which crack into small fragments having sufficient static strength to be used for building material, were developed [3–6]. The major difference between commercial concrete and experimental porous concrete is that porous concrete has a continuous network of aggregates from the bottom to top, which is essential that improves the strength of the basic material [2, 6].

The binary transition metal oxides such as $ZnCo_2O_4$ are low-cost and environmentally friendly. In the structure, Zn occupies tetrahedral site and Co is located at the octahedral site. $ZnCo_2O_4$ is complex and analogous to the Co_3O_4 crystal structure with the replacement of Co^{2+} by Zn^{2+} ions [7]. ZnO, CuO and Al_2O_3 composites with concrete specimen have been shown to have good structural properties and high strength [8-10]. Hence, the cement concrete with $ZnCo_2O_4$ binary oxide admixture will have higher strength and structural properties, which is not reported yet.

British Standard Institution in 2009, ASTM and AASHTO permitted the use of limestone up to 5% in ordinary Portland cement (OPC) as a part of a change to ASTM C150/AASHTO M85 [2, 7]. Still the restrictions that have been investigated both commercially and experimentally are aggregate grading, which controls the porosity and pore size distribution of the microcube. This has a significant effect on the strength as well as the structural properties of porous concretes. In recent days, only a few studies have been focused on the cement with coarse and concrete product conversion development. Mostly glass, recycled glass, steel slag, steel fiber, tires and plastics are used. In concrete admixture, the disposal problems and developments are very difficult compared with commercial technology [5, 6]. However, due to the limitations of greater strength and stability in concrete mixture, different materials have been searched with focus on their physical, structural and mechanical properties for structure development [7]. Consequently, addition of materials like admixture, super-plasticizer cement and nanomaterials has been practically tried to improve the properties of concrete pavement [11–13].

In this study, the introduction of binary nanoparticles, which probably could improve the mechanical and durable properties of cementitious composites has been investigated. Different types of cracks developed in the concrete structure were investigated by SEM. The enhanced strength of nanoparticles incorporated concrete was confirmed through the study of compressive strength. The effect of incorporation of $ZnCo_2O_4$ nanoparticles into the concrete materials has been systematically studied.

2. Experimental Methods

2.1 Synthesis of $ZnCo_2O_4$

For the synthesis of $ZnCo_2O_4$ nanostructures [7], 0.5 M of cobalt nitrate ($Co(NO_3)_2.4H_2O$), and 0.25 M of zinc nitrate ($Zn(NO_3)_2.4H_2O$) were dissolved in 60 mL de-ionized (DI) water and stirred at room temperature for 30 min to achieve the homogeneous solution. To prepare the double hydroxide solution, 1 g of mixed hydroxides (NaOH/KOH) was dissolved in 20 mL of ultrapure water and stirred for 30 min. After that, the two solutions were mixed with continuous stirring for 1 h at 60 °C and maintained for 6 h in an oil bath to ensure the homogeneity of the mixed solution. Finally, the black colour product of $ZnCo_2O_4$ nanoparticles was washed with water and ethanol. The filtered samples were dried on vacuum oven 60 °C for 24 h, after that grained sample was calcined at 300 °C for 5 h.

2.2 Synthesis of $ZnCo_2O_4$ and Admixture with Concrete Specimen

The cement used is the ordinary Portland cement (Grade 43) from the Associated Cement Companies Limited in India. The fine aggregate used is the natural siliceous sand and ASTM C-33 [2]. Drinkable clean water, fresh and free from impurities was used for mixing and curing the tested samples according to the Indian code of practice. The series mixtures were prepared by mixing the coarse aggregates, fine aggregates, cement materials and 5 g of prepared $ZnCo_2O_4$ nanoparticles in a laboratory concrete drum mixer. They were mixed in dry condition for 10 minutes, and 5 minutes after adding the water. Materials of the fresh concrete were observed immediately to maintain the flexural strength following by the mixing procedure. Cube of size 150 mm^3 were cast and compacted for flexural strength tests [14]. Finally, moulds were covered with polyethylene sheets and moistened for 10 h. Then, the specimens were

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demoulded and cured in water at room temperature prior to the experimental procedure. The tensile strength tests of the concrete samples were determined at 28 days. The preparation of the admixtures concrete specimens reported results were the average of three replicates.

2.3 Characterizations and Calculations

The microstructural analysis was performed using SEM (TESCAN VEGA 3) after compression test. The compressive strengths of the concrete mixtures were measured for the 150 mm cube specimens in accordance with BS EN 12390-3 using a digitally controlled compression machine with an extreme load capacity between the ranges of 500 to 700 kN.

Table 1 Ratio of the concrete mixtures with corresponding grade values

Cement	Sand	Aggregate	Grade
1	2	4	Correspond to M-53
1	1.5	3	Correspond to M-53
1	1	2	Correspond to M-53

2.4 Compressive Strengths

The compressive strengths of the concrete mixtures were measured for the 150 mm cube specimens in accordance with BS EN 12390-3 using a digitally controlled compression machine with an extreme load capacity between the ranges of 500 to 700 kN. Before starting the test, any noticeable moisture was detached from the specimens. Thereafter, any movable gravel or any other materials that could be in interaction with the filling plate were cleaned from the specimens of the surfaces. The specimens were then located in the challenging machine perpendicular to the axis of the concrete cast. A constant stacking rate of 0.3 MPa/s was used throughout the tests. The load and vertical dislocation were recorded until the specimen becomes unsuccessful and the maximum load in kN was recorded. These tests were carried out for both the orientation and modified concrete mixes at ages of 7days and $ZnCo_2O_4$ /concrete microcube at different zone after compression test by 28 days. In presence of water, the concrete mixture acquires adhesive & cohesive properties. The hydration of cement and workability are main crucial parameters for the cores microcube. The total water content was ~ 40%-60% by weight of cement. This water is not chemically bound and can be evaporate depending on relative humidity. Porosity of concrete due to evaporating free water and air voids (~1.5% of total volume).

3. Results and Discussion

3.1 Structural Properties

The 3D porous structure was formed by the solid phases of aggregates and cement paste and the pore phase voids are represented by the hollows structure between silica particles. The increase of the structural compactness affects the interaction between porous particles or between the particles and which was considered implicitly in the interaction medium [6]. In other words, the creation of the growth of specimens and the subsequent geometry was taken into account as clearly observed by different resolutions as shown in Fig. 1. In Fig. 2(a,b), $ZnCo_2O_4$ nanoparticles were observed different resolutions with average nanoparticles size 50 nm. Fig. 2(c-d) shows the $ZnCo_2O_4$/concrete microcube at different zone after compression test by 28 days. The developed 3D formation is due to the interaction between $ZnCo_2O_4$ nanoparticles and silica particle, and $ZnCo_2O_4$ particle-wall at aggregations are formed. For the high strength concrete structure, the interface between two aggregate particles was known as sphere-sphere (S-S) and the interface between particle and wall was called sphere-wall (S-W) [15,16]. Mean pore of the specimens studied by 28 days with different size of pores was also estimated. Noticeably large pore size was observed after 28 days specimens with increase in the higher contact surface with strong strengthening properties.

In concrete, “feebler planes” are observed at the interface of the cement sealant and the $ZnCo_2O_4$ nanoparticles aggregate. The micro-cracks that appear at the boundary tend to transmit along the nanoparticle’s aggregate surfaces morphology. These micro-cracks can association to form macro-cracks were influences of the $ZnCo_2O_4$ nanoparticles shown in Fig. 2(c). In accumulation there can be “$ZnCo_2O_4$ nanoparticles aggregate cracks” which run complete the matrix material, as well as “aggregate cracked” which tend split apart the aggregates structure in Fig. 2(d). The internal micro-cracks and micro-voids are reflected by macroscopic stress-strain behaviour of the concrete [17,18]. For uniaxial compression, growth of micro-racks aligns to the direction of stress softening. The steel reinforcement reduces crack widths: stiffening effect on the crack behaviour [19]. For 7 days of compressive test, the surface structure clearly shows weak interaction because of the less formed cracks, very small particles and increased oxygen content. Large porous formation is ascribed to the large number of hydrate groups and aggregated particles as shown in Fig. 2(e). After 28 days of the compressive test, the surface structure clearly seen strong interaction because it has formed length cracks, a smaller number of hydrate groups and aggregated shape of particles of the mixtures concrete (Fig. 2f). After 28 days, the specimens cube strength and density of the $ZnCo_2O_4$ nanoparticles was increased.

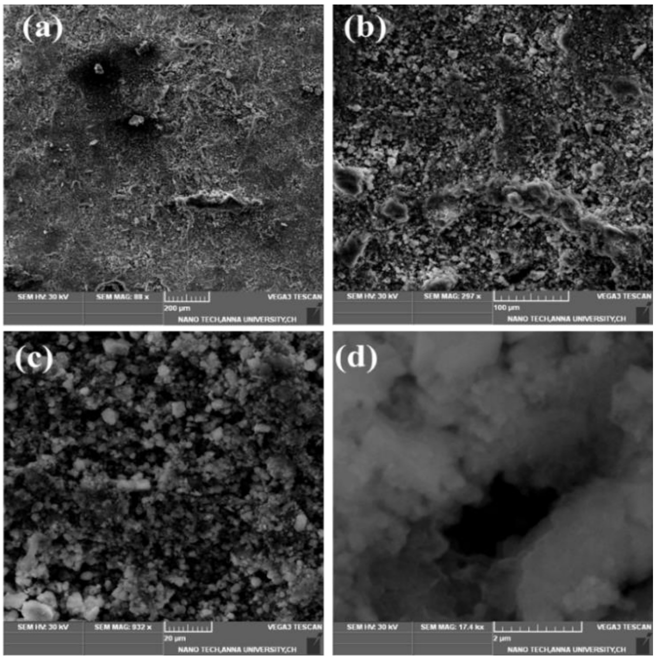

Fig. 1 SEM Images of concrete microcube at different zone after compression test after 7 days

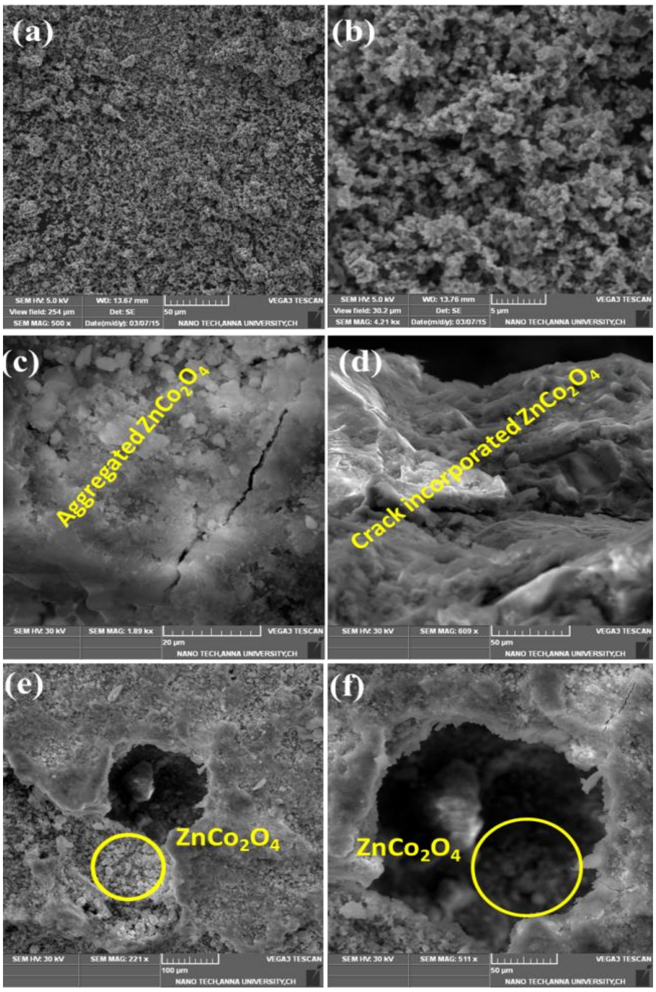

Fig. 2 SEM Images of (a,b) $ZnCo_2O_4$ nanoparticles (c-d) $ZnCo_2O_4$/concrete microcube at different zone after compression test by 28 days

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3.2 Energy Dispersive X-Ray Spectrum

The EDX spectrum shown Fig. 3 confirmed the presence of Zn, Co and O elements with an atomic ratio of zinc (21%), cobalt (38%) and oxygen (41%), during the formation of spinel phase of $ZnCo_2O_4$ nanoparticles.

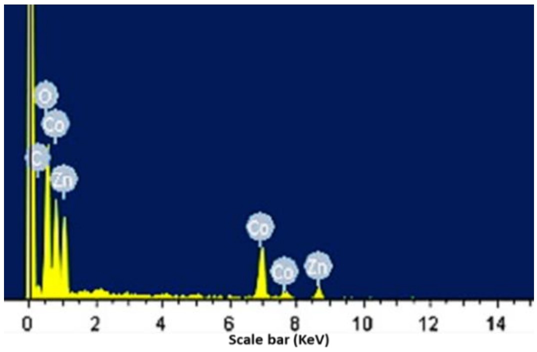

Fig. 3 EDAX spectrum of $ZnCo_2O_4$ nanoparticles

3.3 Investigation of Compressive Strength

Table 2 shows the compressive strength of concrete specimens after 7 and 28 days of compressive test with and without $ZnCo_2O_4$ curing. It was observed that porous concrete (28 days) possess a very different breaking behaviour compared to commercial concrete and 7 days concrete specimens. Each specimen shall be a concrete core with a diameter of 150 mm. Cores shall be through the entire thickness of the porous concrete path. The minimum amount of the core to create a flat surface is perpendicular to the length of the core. Tensile strength is the quantity of flexible stress that a material can resist before failing. Compressive strength is the quantity of compressive strength that a material can resist before failing [19]. The test specimen is exposed to a compressive load to usually from a hydraulic machine recorded until the failure occurs [16]. So, the controlled structural and mechanical characteristics of the microcube possess better strength and density compared with commercial microcube. The increased compressive strength may be due to the large quantity of $ZnCo_2O_4$ nanoparticles present in the admixture. This is important for the excess silica leaching out and producing a deficiency in strength as it replaces part of the cementitious material. The fragmentation performances of different porous concrete admixtures also strongly depend on the aggregate grading.

Table 2 Compression results of the concrete microcube tested after 7 days, and $ZnCo_2O_4$/concrete microcube at different zone after compression tested after 28 days stability

Specimen ID	Age at test	Dimensions (in mm)			Weight (Kg)	Density (Kg/m^3)	Load (KN)	Strength (MPa)
		Length	Weight	Height				
Commercial	28	150.0	150.0	150.0	7.88	2012	414.7	16.32
1303765A	7	150.0	150.0	150.0	8.48	2512	524.7	23.32
1303765B	7	150.0	150.0	150.0	8.51	2522	544.5	24.20
1303765C	7	150.0	150.0	150.0	8.53	2528	599.2	26.63
1303765D	28	150.0	150.0	150.0	8.48	2512	789.5	35.09
1303765E	28	150.0	150.0	150.0	8.57	2539	747.2	33.21
1303765F	28	150.0	150.0	150.0	8.59	2545	732.2	32.54

4. Conclusion

$ZnCo_2O_4$ nanoparticles were synthesized by co-precipitation method. The concrete specimens were prepared with and without incorporating $ZnCo_2O_4$ particles and subjected to compression test after 7 and 28 days. The influences of $ZnCo_2O_4$ nanoparticles on durability and compression properties of concrete specimens were experimentally investigated. It was observed that porous concretes have a very different breaking behaviours compared to commercial concrete. SEM images showed the cracking patterns of porous concretes providing insights on the material performance. In porous concretes, cracks are required to propagate into locations indicated by the aggregate microstructure and the pore distribution. The compression test showed higher strength of the concrete obtained by completely filled $ZnCo_2O_4$ nanoparticles on porous concrete with the cement paste. The results showed enhanced strength of the porous concrete microcubes for safety applications that required a numerous fragmenting cementitious material and can be used for different environmental risks like typhoon, raining, and earth quake with long life.

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