Diyala Journal of Engineering Sciences

Journal homepage: https://djes.info/index.php/djes

ISSN: 1999-8716 (Print); 2616-6909 (Online)

Investigation the Influence of adding Nano –Yttria Partially Stabilized Zirconia (NZrO2-5wt%YPSZ) on the Physical and Mechanical Properties of Concrete

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ARTICLE INFO

Article history:
Received January 8, 2023
Revised July 23, 2023
Accepted August 29, 2023
Available online September 1, 2023

Keywords:
Nano Zirconia
Building materials
Nanoparticles
Tensile strength

ABSTRACT

Building materials showed remarkable progress, as many methods were used to enhance their properties, such as nanomaterials which have played a major role in this field. This research reveals the complex integration of nano-zirconi (NZrO2-5wt%YPSZ). as with concrete and its effect on the different mechanical properties. The main objective of this research is to reduce the porosity of concrete by adding doses of nano-zirconia to the concrete mixture to enhance the microstructure, which enhances its mechanical properties. The results showed that the addition of nano-zirconia decreased concrete slump, and also increased the rates of absorption and porosity due to the agglomeration of nanoparticles. The compressive strength increased to reach 30, 47.5, and 60 MPa at the ages of 7, 28, and 90 days, respectively. The splitting tensile strength increased when the zirconia content was increased, reaching its highest level when substituting 0.7wt% when compared with the reference mixture. In summary, the current study sheds light on the effect of nano-zirconia on the mechanical properties of concrete by filling the pores, which enhances its microstructure because it reshapes the complex texture of the concrete mixture.

1. Introduction

The manufacturing of ordinary portland cement (OPC) on a global scale leads to considerable CO_2 emissions, the introduction of Green concrete in the mix design can help regulate the CO_2 emissions during cement and concrete manufacturing without compromising the final product's quality, One effective solution to address this world wide concern is the incorporation of supplementary cementitious materials as additives to cement, including the use of nanoparticles.[1] Nanotechnology has added a new vision and expectations in the world of civil engineering in terms of the ability to control the properties of building materials, the most important of which is ordinary portland cement [2] The rapid development in the building materials industry, along with the application of nanotechnology, has led to the improvement of the microstructure and homogeneity of particle size in concrete. This reduces the porosity of concrete, thereby enhancing its durability and performance [3].The utilization of nanomaterials in concrete offers several advantages in enhancing certain mechnical

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DOI: 10.24237/djes.2023.16305

properties of cement-based materials, despite some drawbacks like increased water demand. Nano silica, alumina, titanium oxide, and zirconia oxide are some of the nanomaterials commonly employed, the expected outcomes of incorporating nanomaterials in concrete include pore diameter reduction, as well as improvements in strength and durability of the concrete[4].Due primarily to their small size and large surface area, nano-materials can significantly improve the mechanical and physical characteristics of concrete, Nanoparticles serve as filler materials between the larger cement particles, thereby enhancing the interfacial bond strength and reducing the porosity of concrete. Additionally, the small size of nanoparticles makes them highly efficient additives for modifying cement mortar[5]. The main cause of the use of nanoparticles in traditional building materials, It is to obtain strong and lightweight compounds that improve the physical and mechanical properties of cement when adding in appropriate quantities with a slight decrease in the ability of concrete, the most widely used materials are nano-zirconia and nano-alumina, which improve the mechanical and physical properties of concrete[6]. In various studies, it has been documented that incorporating zirconia oxide nanoparticles in ordinary portland cement (O.P.C) as partial replacement leads to a substantial increase in split tensile strength, and overall concrete strength, This enhancement is attributed to the rapid consumption and release of $Ca(OH)_2$ during cement hydration, facilitated by the high reactivity of zirconia particles ZrO_2Consequently, cement hydration is accelerated, resulting in the generation of abundant hydration products, improved packing density of cement particles, and a reduction in the volume of large pores within the cementing paste[7] Several studies have evaluated the effect of adding different types of nanomaterials, such a s ZrO_2, SiO_2, Al_2O_3, and $CaCO_3$, at varying ratios (1%, 1.5%, 3%, and 5%) as partial substitutes for ordinary Portland cement to enhance the compressive strength of concrete, According to the findings of these studies, the addition of nanoparticles to cement increases the compressive strength of concrete compared to ordinary concrete[8]. The properties of concrete can be enhanced through various methods, including the use of concrete nanomaterials (NM), which can improve concrete pore structures, accelerate the formation of C-S-H gel, and enhance mechanical properties. For instance, fly ash significantly improves concrete strength and durability. Nano-Silica addresses early-stage low-resistance issues by improving concrete density and structure, Nano iron enhances compressive strength[9]. In recent years, researchers have been interested in the use of various nanomaterials for concrete reinforcement, including Nano silica (NS) - Nano-SiO_2, Nano Calcium Carbonate (NC) - Nano-$CaCO_3$, Nano alumina (NA) - Nano-Al_2O_3, Nano- Iron oxide (NF) – Nano - Fe_3O_4, Nano titanium dioxide (NT) - Nano-TiO_2, Nano Zinc oxide (NZ) - nano-ZnO_2, Nano- ZrO_2-Nano-Limestone, Carbon Nano Tube, and nano methacholine. These nanomaterials act as cementitious components to enhance the properties of concrete, By reducing the cement content and filling voids in the material, it greatly improves the performance of traditional concrete[10]. In this study, the impact of incorporating nano (NZrO_2-5wt%YPSZ) on the physical and mechanical properties of concrete was investigated. Various percentage (٠.3,0.5,0.7) wt% were added, based on their effectiveness in previous studies, and different curing ages (7,28,52) days were considered to assess their influence at both early and later stages.

2. Materials and methods

2.1 Cement

Cement is a substance with adhesive and cohesive properties that binds mineral fragments together. It is primarily produced from calcareous materials like limestone or chalk, alumina and silica from clay or shale, and marl, a combination of calcareous materials, the manufacturing process involves grinding raw materials, mixing them, and subjecting them to high temperatures of up to approximately 1450 °C in a large rotary kiln, resulting in clinker. The clinker is then cooled and finely ground into a powder, with gypsum added [11].Cement production significantly contributes to CO_2

emissions and solid waste generation,the dry manufacturing process accounts for 40% of CO_2 emissions, mainly due to fossil fuel combustion in kilns, the remaining 50% comes from limestone roasting[12]. In this study, ordinary portland cement (O.P.C) has been used. According to Iraqi Specification No.5 / 2019, the physical and chemical characteristics of the cement used detailed in Tables 1 and 2.

2.2 Coarse aggregate

The greatest volume of the mixture and a crucial component in the manufacturing of concrete is coarse aggregate. Based on several variables, including the size and grading specifications for the concrete mix and the intended shape of the concrete element being poured[13] .This study utilized aggregate with a maximum particle size of 19 mm. According to Iraqi Standard No. 45/1984, aggregate grading has been established. Table (3) shows chemical properties of coarse aggregate used in this study.

2.3 Fine aggregates

Sand, commonly referred to as fine aggregate, is an essential ingredient in the creation of concrete. The cement paste, which fills the spaces between the bigger aggregate particles, is created when it reacts with cement and water. The use of fine aggregate improves the concrete mixture's workability and contributes to the final concrete product's desired consistency and strength.[13]

Natural sand with a maximum grain size of 5 mm is used. Table (4) displays the chemical characteristics of sand that meet Iraqi Specification No. 45/1984.

Table 1: Experimental physical properties of O.P.C

Physical Properties	Results	IQS No. 5/2019
Setting Time (Vicat's Method)	190m 4h	Primary (Minimum=45m Final (maximum=10h
Fineness (Blaine Method), m^2/kg	258	>250
Compressive Strength, MPa	2days=14.6 28 days=42.5	——

Table 2: Experimental chemical composition of O.P.C

Compound	Chemical formula	Test Results %	IQS No.5 /2019
Silica	SiO_2	23.82	--------
Alumina	Al_2O_3	5.60	--------
Iron Oxide	Fe_2O_3	5.55	--------
Lime	CaO	66.92	--------
Magnesia	MgO	3.02	Max5
Sulphate	SO_3	2.45	Max 2.5 ifC3A<5 Max 2.8 ifC3A>5
Insoluble Residue	I.R	1.02	Max 1.5
Loss on Ignition	L.O.I.	3.5	Max 4
Tricalcium Aluminates	C3A	5.45	Max 3.5
Tricalcium Silicate	C3S	38.78	--------
Dicalcium Silicate	C2S	39.12	--------
Tetra calcium Alumina Ferrite	C4AF	16.9	--------

Table 3: Experimental chemical Properties for aggregates

Chemical Properties	Results	IQS No. 45/1984
Sulfate Content	0.001	Max.3
Clay Content	0.06	Max.0.1

Table 4: Experimental chemical properties for fine Aggregates

Chemical Properties	Test Results	IQS No. 45/1984
Sulfate Content	0.07	0.5-0.75
Clay Content	2.89	Max.5

2.4 Water

For mixing and processing in this study, tap water was used and a water-to-cement (w/c) ratio (0.48).

2.5 Zirconia nanoparticles (NZrO$_2$-5wtYPSZ)

Zirconia (ZrO_2) nanoparticles have been used in concrete to enhance its properties. They are added as a partial replacement for cement in an amount of up to 2% by weight of cement. The rapid reaction between the calcium hydroxide and the nanoparticles results in the formation of additional hydration of the cement, which helps in improving the mechanical pro perties, especially compressive strength, splitting resistance, and flexural strength. However, the addition of nano ZrO_2 also reduces the workability of concrete [6]. Table 5 presents the physical properties and chemical composition of nano zirconia partical. Mixing ratios (0.3, 0.5, 0.7) wt% were adopted as a partial replacement for cement, based on previous research[6, 14, 15].

Tables 5: Shows the physical properties and chemical composition of (NZrO$_2$-5wtYPSZ)

Chemical composition		Physical Properties	
ZrO_2	91$\pm$ 0.2	Appearance	White nano powder
Y_2O_3	8.5$\pm$0.2	Purity	Y_2O_3-8 .6 - 9.0%
Fe_2O_3	<0.002	Average particle size (APS)	20~35 nm
Na_2O	<0.005		
Al_2O_3	<0.1	Morphology	Spherical
CaO	<0.002		
SiO_2	<0.005		

2.6 *Weight and mixing rates for nanoparticles*

Nano Zirconia powder (NZrO2-5wt% YPSZ) (NZY), manufactured by Sky spring nano Materials, Inc. was precisely measured according to specified proportions to partially replace the weight of cement in the concrete mix. This was carried out in comparison to the reference sample (Ref). The specific weights of each component are listed in Table (6).

Table 6: Mix proportions of concrete samples

Nano Zirconia Samples	Nano Oxide (wt%)	Cement (kg/m^3)	Nano Oxide (kg/m^3)	sand (kg/m^3)	Gravel (kg/m^3)	Water (kg/m^3)	w/c
Ref1	0	395	0	717	1020	190	0.48
NZY1	0.3	393.815	1.185	717	1020	190	0.48
NZY2	0.5	393.025	1.975	717	1020	190	0.48
NZY3	0.7	392.235	2.765	717	1020	190	0.48

2.7 Porosity

During the experiment, the sample was immersed in water for a duration of 28 days. Following this, the sample was submerged 25 times in water to remove any air bubbles. The sample was then weighed while still immersed in water using an electronic balance. Next, the sample was taken out of the water and carefully dried on its outer surface using a cloth before being weighed again. Subsequently, the sample was placed in an electric oven at a temperature of 110 °C for twinty four hours. After removing it from the oven, the sample was weighed once more. The porosity rate was then calculated using Equation (1) specified in the ASTM standard C642-13[16].

$$porosity\ (\%) = ((W2 - W1)/(W2 - W3)) * 100 \quad (1)$$

Where:

W1; The mass of the sample after it has been dried in an oven and is in contact with air(g) .

W2; The mass of the sample after its surface has been dried and is in contact with air, following immersion in water(g) .

W3;The sample's apparent mass while immersed in water (g).

2.8 Absorption

The water absorption of all samples was evaluated in the form of cubes measuring (100 x 100 x 100) mm at 28 days, according to ASTM C642-13 [16]. The samples were initially placed in an oven at 100 °C for 24 hours. After cooling, the dry weight of each sample was determined using an electronic balance. Following that, the samples were immersed in water at 20-25 °C for 24 hours before being weighed again after surface drying. Finally, Equation (2) was used to calculate water absorption.

$$Water\ absorption\ (\%) = \left(\frac{W2-W1}{W1}\right) * 100 \quad (2)$$

3.*Concrete Mix Design*

3.1 Casting and testing of specimens

The concrete was mixed at temperature, approximately 20-25°C. The cement was manually mixed with the nanomaterials for a period of 2 to 3 minutes, to prevent volatilization, it is recommended to limit the duration of mixing nanomaterials with cement. as shown in Figure (1). Both fine and coarse aggregates were mixed in the concrete mixer. Subsequently, all dry ingredients were mixed in the mixer for approximately 5 minutes. Following that, the water-to-cement (w/c) ratio (0.48) was added to the dry ingredients, and the ingredients were mixed for an additional 5 minutes until the fresh concrete was obtained. to prevent the samples from sticking to the mold's wall, the inner surface of the mold is lubricated with oil before pouring the concrete mixture. After 24 hours, the samples were carefully taken out of the molds and placed in a water tank for curing. The casting process utilized metal molds of different shapes, including (cylindrical and cubic) specimens were tested on 7, 28 and 90 days.

Figure 1. Manual mixing cement with nano zirconia

3.2 Mechanical tests

- Compressive strength tests were showed in accordance with British Standard 1881 part 116: 1983[17]. All cubes were tested using an ELE digital testing machine with a 2000 kN hydraulic compressive force. In this test, concrete cubes with dimensions (100 * 100 * 100) mm were used, and they were treated for three ages (7,28,90) days. All specimens were stored in water until the testing period had expired. as shown in Figure (2).

Figure 2. Shows compressive strength test

- The splitting tensile strength was determined according to the procedure outlined ASTMC496/C496M[18]. In this test, cylindrical concrete samples with dimensions (300 * 150) mm were used. This test was performed on concrete samples after 28 days. as shown in the figure (3).

Figure 3. Shows splitting tensile strength test

4. Results and discussion

4.1 Workability

In Figure (4) a noticeable difference in the workability of concrete is observed. The results indicate that the optimal ratio of addition for nano-zirconia is (0.5), and when the ratio is increased to (0.7), the workability of concrete decreases significantly. This decreases in workability can be attributed to the spherical shape of the nano-zirconia particles, which have a specific surface area. As the percentage of addition increases, the surface area exceeds the required threshold leading to an increased demand for water. Consequently, the concrete's ability to absorb water increases and the workability of concrete decreases [6, 19].

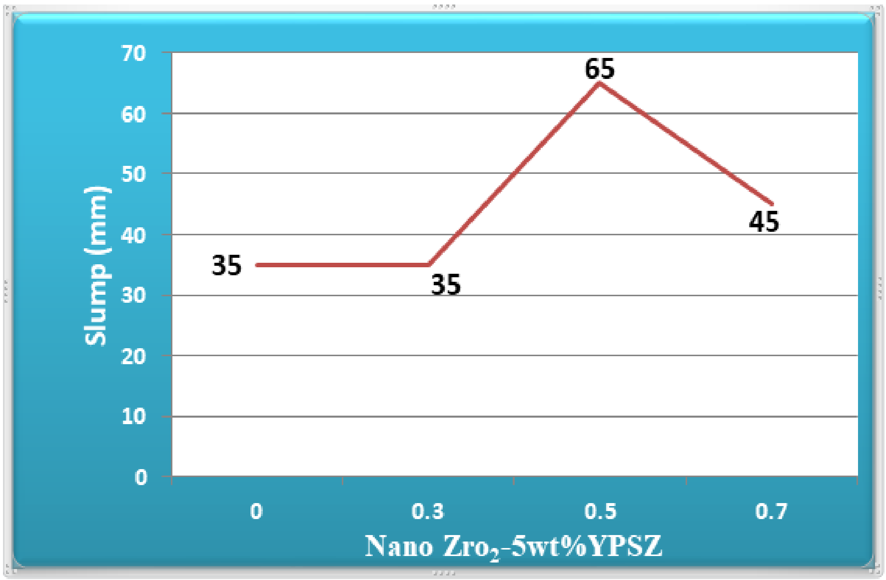

Figure 4. Shows the workability of concrete for different ratios of ($NZrO_2$-5wtYPSZ)

4.2 Porosity

Figure (5) illustrates an increase in the porosity of the concrete after the addition of nano material, particularly at the 0.3% dosage. This can be attributed to the accumulation of nanozirconia, leading to the formation of weak areas that subsequently transform into larger pores [13].

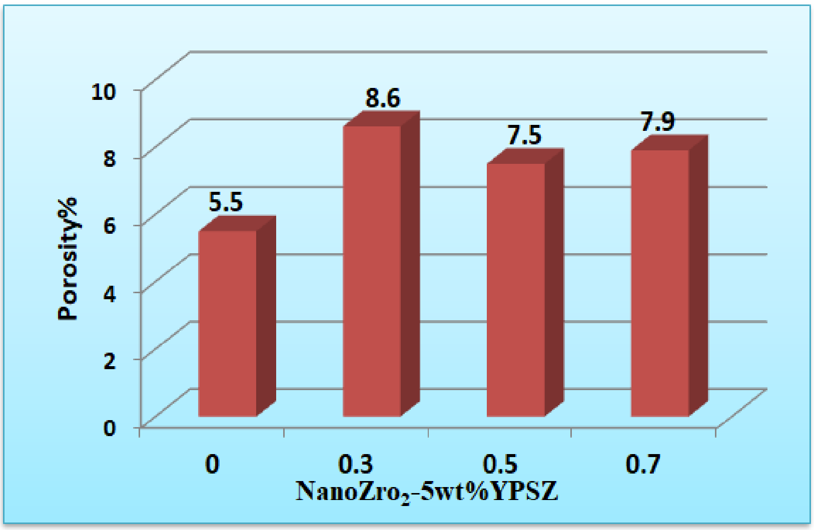

Figure 5. Porosity results for different mixtures of ($NZrO_2$-5wtYPSZ)

4.3 Absorption

Figure (6) shows an increase in the absorption rate after adding the nanomaterials as a result of the increase in porosity after the occurrence of the phenomenon of agglomeration of nanoparticles, which was mentioned. Table (7) shows a comparison between the physical properties of concrete with addition (NZY) with the reference sample (Ref) for different ages.

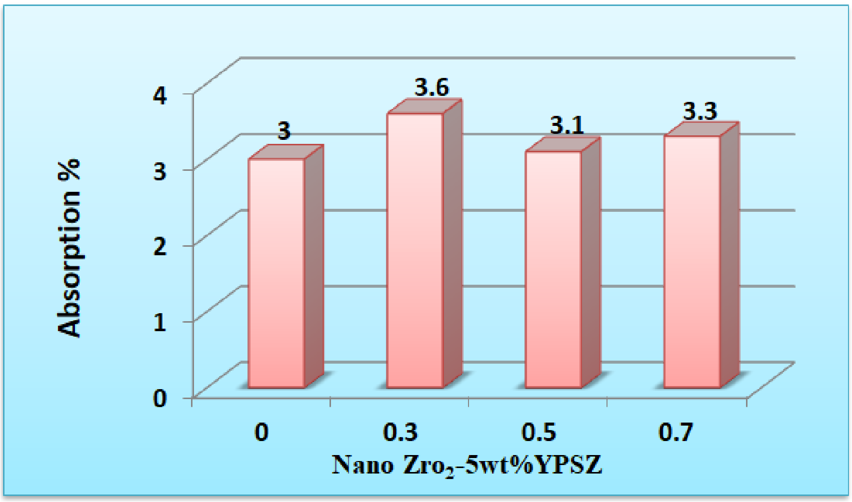

Figure 6. Absorption results for different mixtures of ($NZrO_2$-5wtYPSZ)

Table 7: Results of physical tests for different ages

Zirconia Samples	Added percentage %	w/c	Workability mm	Porosity%	Absorption rate%
				90 days	90 days
Ref1	0	0.48	35	5.5	3
NZY1	0.3	0.48	35	8.6	3.6
NZY2	0.5	0.48	65	7.5	3
NZY3	0.7	0.48	45	7.9	3.3

4.4 Compressive test results

Figure (7) shows a slight improvement in compressive strength for samples containing nano-zirconia at different ages. This slight improvement is attributed to the absence of excess hydration products from calcium silicate hydrate (C-S-H), which normally contribute to increased strength. The absence of these products is due to the non-displacement of nano-sized particles (20–45 nm) in the cement matrix due to agglomeration, which results in voids[20]. As a result, the porosity of the concrete increased, which led to a higher rate of absorption, and this phenomenon is supported by the analysis of Field Emission scanning electron microscopy (FE-SEM) shown in Figures (8,9) The microstructure comparison between the reference sample and the sample containing (NZY) is illustrated in Figure (10) and Figure (11) shows the distribution of nano-zirconia particles in the concrete sample through an image Energy dispersive x-ray test (MAPING EDX).

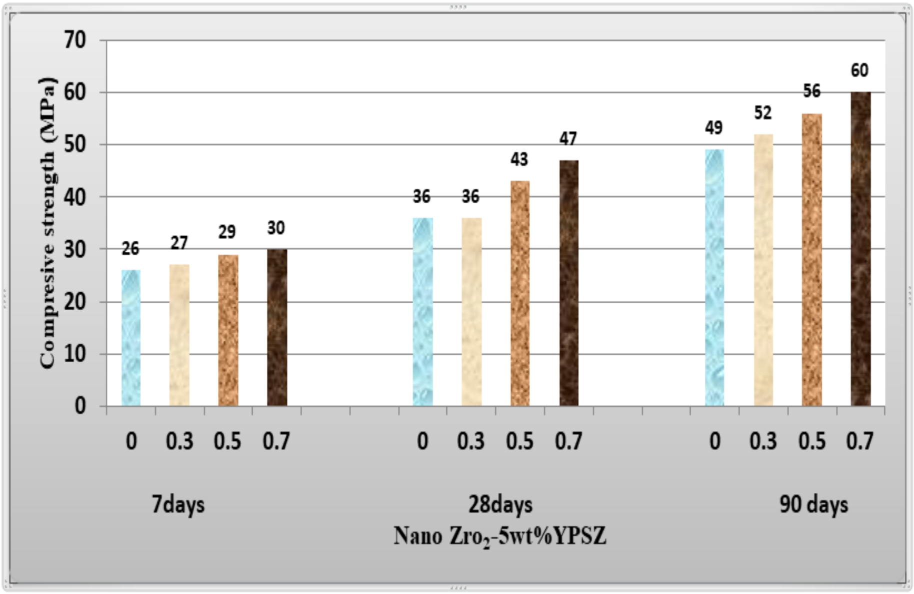

Figure 7. Compressive strength results for different mixtures of ($NZrO_2$-5wtYPSZ)

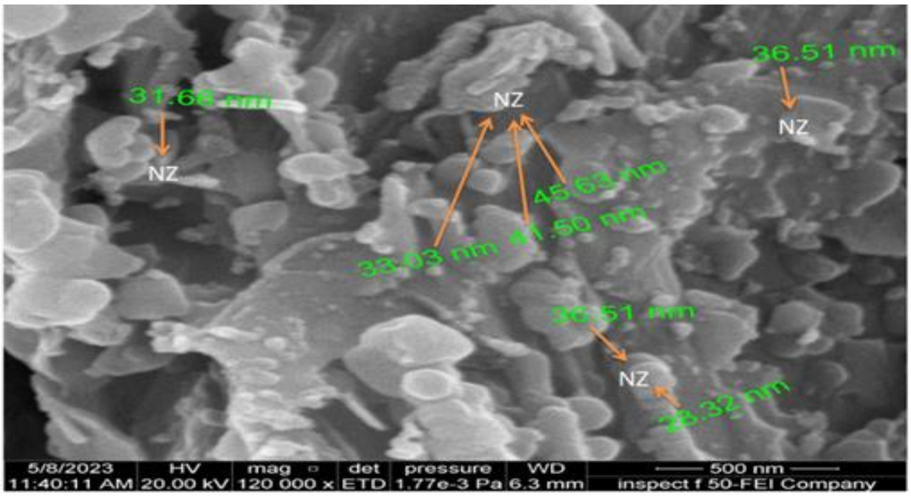

Figure 8. FE-SEM images of ($NZrO_2$-5wtYPSZ) in concrete

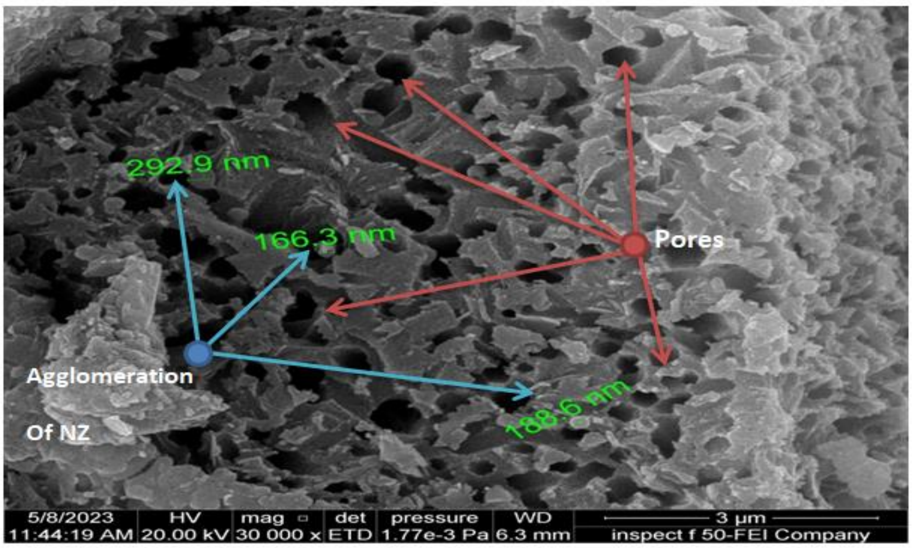

Figure 9. FE-SEM images of pore and agglomeration of ($NZrO_2$-5wtYPSZ) in concrete

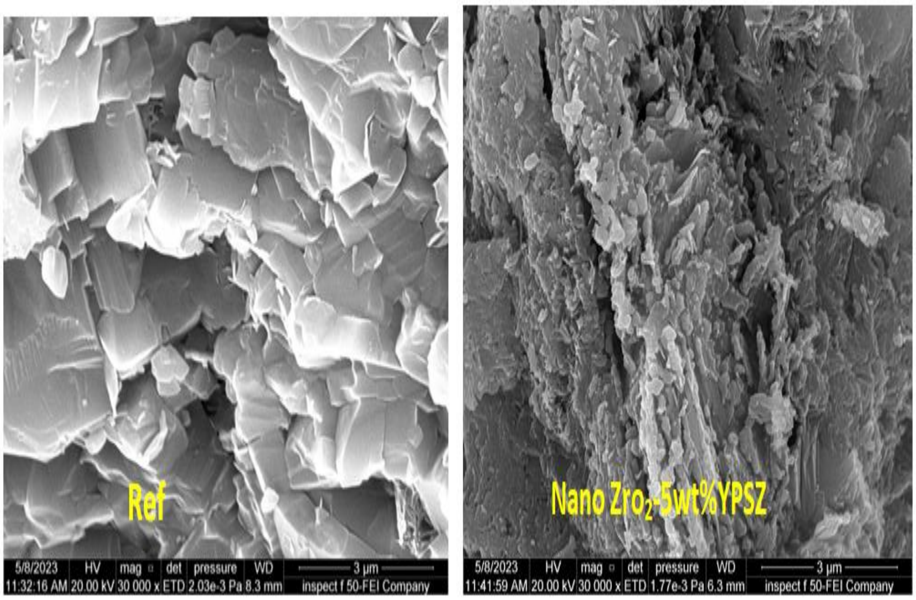

Figure 10. FE-SEM images illustrates the difference in microstructure between the reference sample and the sample containing (NZrO$_2$-5wtYPSZ)

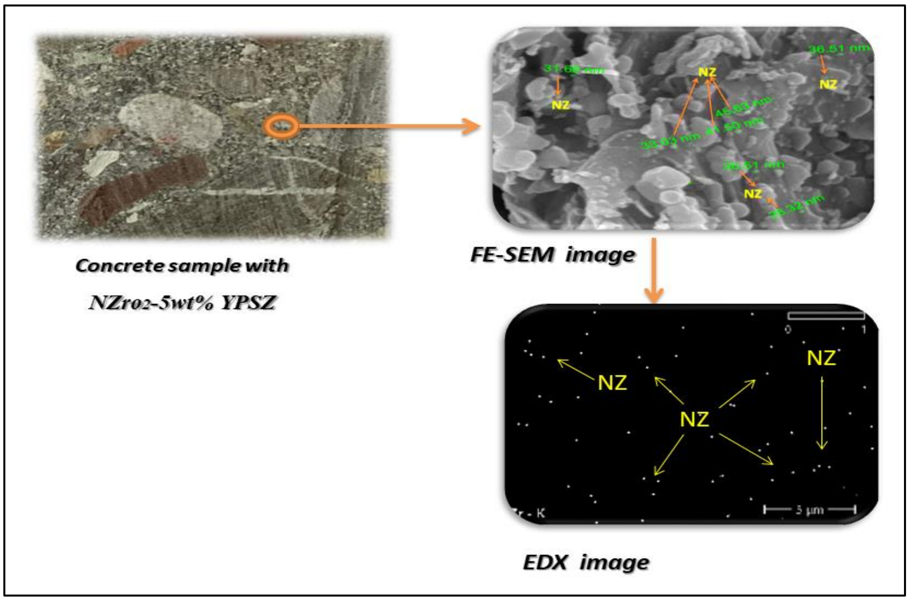

Figure 11. FE-SEM and EDX image showing the distribution of zirconia nanoparticles in the concrete sample

4.5 Splitting tensile test results

Figure (12) depicts the splitting tensile strength, which follows a similar trend as the compressive strength. The concrete specimens containing Nano ZrO$_2$ powder exhibit higher splitting tensile strength compared to the control specimen. Furthermore, the splitting tensile strength demonstrates an incremental improvement with an increasing concentration of Nano ZrO$_2$ powder, reaching its peak enhancement at 0.7%The presence of nano ZrO$_2$ powder plays a significant role in filling the capillary pores between the hydrated cement paste and aggregate, leading to the observed increase in splitting tensile strength. This filling effect causes densification in the interfacial zones between the concrete components, resulting in higher density. Consequently, both the compressive and splitting tensile strengths experience an enhancement [19]. Table (7) shows a comparison between the mechanical properties of concrete with addition (NZY) with the reference sample (Ref) for different ages

Table 8: Results of mechanical tests for different ages

Zirconia Samples	Added percentage %	compressive strength MPa			Splitting Strength (MPa)
		7days	28days	90 days	28days
Ref1	0	26	36	49	3.3
NZY1	0.3	27	36	52	3.2
NZY2	0.5	29	43	56	3.8
NZY3	0.7	30	47	60	4

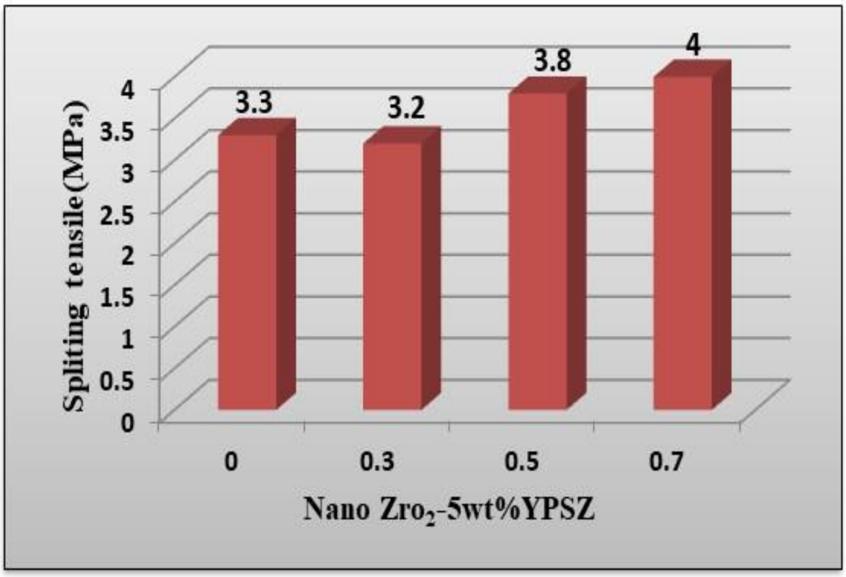

Figure 12. Splitting tensile strength results for different mixtures of ($NZrO_2$-5wtYPSZ)

6. Conclusions

1. Analysis of the microscopic image (FE-SEM) unveiled a notable increase in the number of pores of the concrete sample containing nano-zirconia ($NZrO_2$-5wtYPSZ)) which were formed as a result of the agglomeration of the nano-material when mixed with cement.
2. Compressive strength was low at all ratios at early ages (7) days, then it started to increase at late ages (28 and90) days.
3. Optimal mechanical properties of the concrete were attained when nano-zirconia was added at a ratio of 0.7wt%.
4. The mechanical properties of the concrete showed minimal variation when ($NZrO_2$-5wtYPSZ) was added in the range of 0.5% to 0.7%. This slight improvement could be attributed to the formation of weak regions, possibly due to inadequate dispersion of nanoparticles within the cemente.
5. The (FE-SEM) analysis of the concrete sample containing nanomaterials exhibited notable disparities in its microstructure compared to the reference sample. These disparities were attributed to the formation of additional products from the (C-S-H) gel.
6. To achieve an optimal dispersion and avoid nanomaterial agglomeration in cement, it is essential to follow a suitable mixing technique.
7. The increase in absorption rate and porosity, in contrast to the reference sample, can be ascribed to the agglomeration phenomenon resulting from the heightened surface activity of nanoparticles.

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