ENHANCEMENT OF MECHANICAL PROPERTIES OF CEMENT MORTAR USING ZEOLITIC IMMIDAZOLATE FRAMEWORKS (ZIF-8) AS AN ADMIXTURE

FINAL YEAR PROJECT UG 2019

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ABSTRACT:

Nanomaterials have been used in improving strength of cement mortar and concrete as cementitious composites have high compressive strength and low ductility and toughness. Cementitious composites have nano pores in cement matrix which reduces the strength and these pores if filled with nanomaterials could increase the compressive strength. Many nanomaterials have been used to enhance the properties of cement matrix, but no research has yet been published on ZIF-8.

ZIF-8 is a class of nanomaterials extracted from metallic oxide frameworks (MOFs) which closely resembles zeolites. Zeolites along with other nanoparticles like Titanium Dioxide, Boron Nitride etc, have shown remarkable increase in mechanical and durability properties of cement mortar. In this project, ZIF-8 was added in cement mortar as an admixture to investigate its performance. The results are compared with other nanoparticles like zeolites, Carbon Nano-Tubes (CNTs) and Titanium Dioxide. Since physical properties (compound structure similarity) of ZIF-8 are similar to zeolites, a positive effect on its mechanical properties is observed. At elevated temperatures, ZIF-8 framework loses its Zn atoms and breaks down to 3D carbon chains retaining their morphology which could act as carbon nanotubes but with less tensile strength.

DEDICATED TO OUR PARENTS AND TEACHERS

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CERTIFICATE

This is to certify that the

Final Year Project Title

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INTRODUCTION:

In recent years, nanotechnology has been used to improve the performance of concrete in different aspects. Different researchers have conducted studies in the field of nanomaterials with concrete and cement mortar and have observed positive effects on their performance.

ZIF-8 (Zeolitic Imidazolate Framework, $Zn(C_4H_5N_2)_2$) is a metal organic framework (MOF) made by zinc ions coordinated by four imidazolate rings in the same way as Si and Al atoms are covalently joined by bridging oxygens in zeolites. The sphere represents the pore size within the framework which is used for gas storage. The structure of ZIF-8 is shown below.

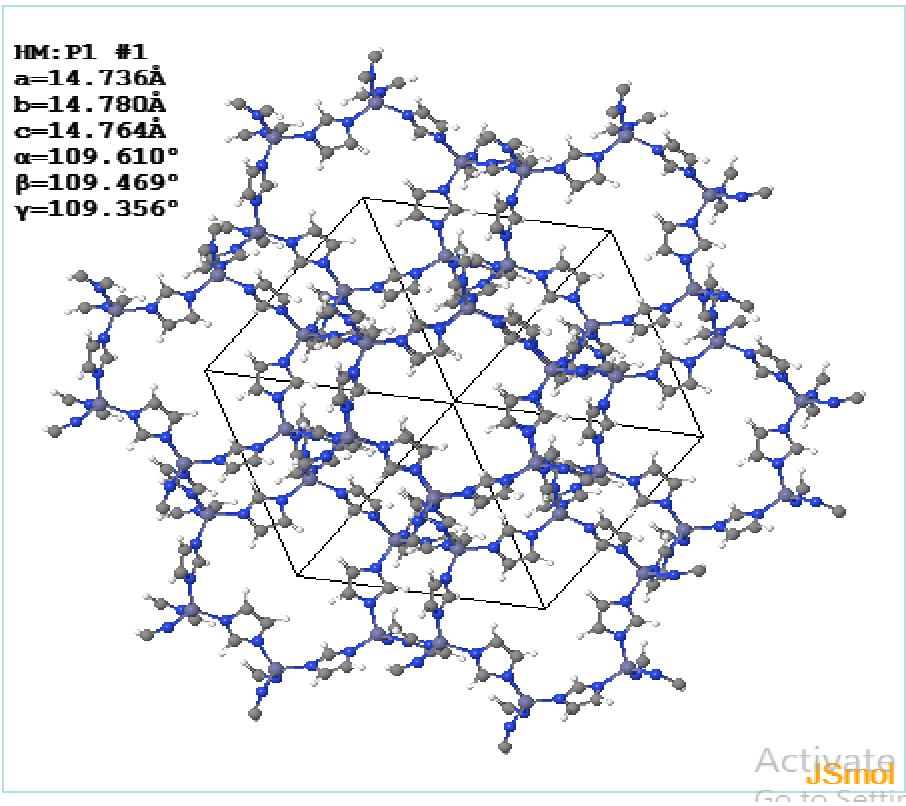

Figure 1: Structure of ZIF-8 crystal

Size and shape of the ZIF-8 nanoparticles depends on mixing process of raw materials. Lowering temperatures increases the number of nuclei during the nucleation process. Ratios of concentrations of raw materials affect the particle growth process. The ZIF-8 nanoparticles have high gas adsorption properties, that’s why they are used in gas capturing membranes.

Due to their robust porosity, resistance to thermal changes, and chemical stability, ZIF's are being investigated for different applications such as bio-membranes and carbon capture. ZIFs on further thermal processing yield carbon chains which are very stable like ZIFs.

OBJRCTIVES:

- Study the effect of ZIF-8 nanoparticles on compressive strength of cement mortar
- To determine optimum content of ZIF-8 for cementitious composites
- Assessment of results in terms of industrial use

LITERATURE REVIEW:

No scientific study has been published on interaction of ZIF-8 nanoparticles with cement mortar or concrete. So, keeping in view of properties of nanomaterials which have already been used as nano-admixture in concrete or cement mortar, we are conducting a scientific study on interaction of ZIF-8 with cement mortar.

Firstly, two relevant studies are discussed below. These studies pertain to admixing of two nanomaterials namely CNTs and Nano-titanium dioxide. Secondly, a study is presented which discusses relevant properties of ZIF-8 nanoparticles.

Interaction and effects of Carbon Nanotubes in cement mortar:

Properties of Nanomaterial:

Multi-walled CNTs after modified by H_2SO_4 and HNO_3 mixture solution were added to cement matrix composites. CNTs have very high theoretical strength with high thermal and chemical stability.

Table 1: Properties of CNTs

External Diameter	10-30 nm
Length	0.5-500 microns
Purity	95%

Specific Surface Area	40-300 m^2/g

Properties of Cement Matrix Composites:

OPC was used in addition to fine particles of specific gravity 2.62 from natural standard sand. Water to cement ratio w/c was 0.45 with mixture composition of 0.45:1:1.5 (Water : Cement : Sand). The CNTs were added in the amount of 2% by weight of cement.

Results:

28-day compressive strength of 40x40x160 mm specimens was increased up to 19% while flexural strength was increased up to 25%.

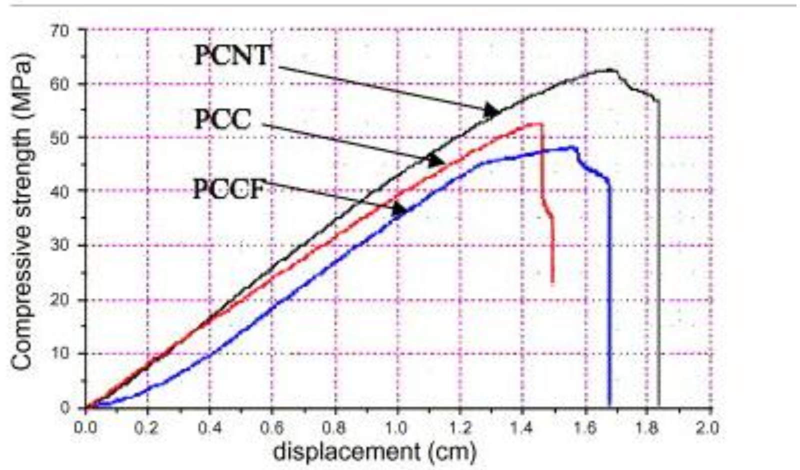

Figure 2:Typical load displacement curve of cement matrix composite

Conclusion:

The strength enhancement and matrix improvement were attributed to the bridging effect and filling effect of CNTs due to their nano-scale size.

Interaction of Nano-Titanium Dioxide with Cementitious Composites:

Properties of Nanomaterial:

Nano TiO_2 powder was used. It has a particle size of 10-20 nm, specific surface area is 20-30 m^2/g with purity of 99%.

Properties of Cementitious Mixture:

OPC type-1 was added with natural sand of size less than 4.75mm in 1:3 proportions. And w/c ratio of 0.5 was used. Nano TiO_2 was added in following ratios of weight percentage of cement: 0.25, 0.75, 1.25 and 1.75. No other admixture was used.

Results:

50x50x50 mm cubes were casted by first admixing method i.e. the admixture was mixed in water first and then remaining casting was resumed. Stirring time of 2 minutes plus ultrasonic dispersion was applied for 20 minutes. 28-day compressive strength was increased by 4.26-19.33% for different percentages of Nanotitanium with 0.75% of NT by cement being the optimum.

Table 2: Compressive testing results of TiO2

Name	TiO2 %	7 days (MPa)	Enhanced extent (%)	28 days (MPa)	Enhanced extent (%)
CM0	0	11.21	-	29.13	-
NM1	0.25	14.85	32.47	32.19	10.50
NM2	0.75	16.78	49.68	34.76	19.33
NM3	1.25	15.93	42.11	33.52	15.07
NM4	1.25	14.69	31.04	30.37	4.27

Conclusion:

The strength enhancement was attributed to decrease in porosity of matrix by the filling effect of Nanotitanium. Nucleation effect and bridging effect were also cited as the cause of matrix improvement in the review “Multifunctional cementitious composites modified with nano titanium dioxide: A review” by Zhen Li et al.

Interaction of nano-zinc dioxide with cement mortar:

Properties of nanomaterial:

The nano-particle used in this study was nano-Zinc oxide (NZno) with the average particle size of 60nm.

Table 3: Properties of nano ZnO

Average particle size	*Specific surface area (m^2/g)*	*Density (g/cm^3)*	*Purity (%)*	*Appearance*
60 nm	18	0.25	>99.5	White

Properties of cementitious mixture:

A cement mortar mix 1:2 was used to prepare the test samples. The water to binder (Cement + Nano-ZnO) ratio for all mixtures was fixed at 0.35. 1% superplasticizer was added in mixture by weight of cement. Nano-ZnO was added in percentages of 0%, 1.0%, 3.0% and 5.0% by weight of cement.

Results:

7.6 × 7.6 × 7.6 cm cubes were casted.

Table 4: Compressive and Split tensile strengths os samples of nano ZnO

Sample label	*Compressive Strength (MPa) 28th Day*		*Split Tensile Strength (MPa) 28th Day*	
	Target	*% of enhancement*	*Target*	*% of enhancement*
CM	*41.12*	-	*2.07*	-
NZ1	*48.15*	*17.09*	*3.10*	*49.75*
NZ3	*50.63*	*23.12*	*3.34*	*61.35*
NZ5	*49.65*	*20.74*	*3.26*	*57.48*

Conclusion:

The strength enhancement was reported because of nucleation and filling effects in cement matrix.

Relevant properties of ZIF-8 crystals

Size:

Room temperature synthesis yields ZIF-8 crystals of size ranging from 30-90 nm depending on mixing time.

Porosity:

"An important structural feature of these two ZIFs is that they possess large pores (11.6 and 14.6 Å in diameter for ZIF-8 and -11, respectively) connected through small apertures (3.4 and 3.0 Å across for ZIF-8 and -11, respectively). The pore sizes are approximately twice as large as those of their zeolite counterparts."

Thermal and Chemical stability:

ZIF-8 crystals show highly desirable properties such as chemical and thermal stability and high surface area. "ZIF 8 crystals have high thermal stability (up to 550°C), and remarkable chemical resistance to boiling alkaline water and organic solvents"

Specific Surface Area:

It has a high specific surface area ranging from 400 m^2/g to 800 m^2/g.

Applications of ZIF-8:

- Due to their tunable pore size, they have been successfully used for carbon capture. One liter of ZIF-8 can hold 83 liters of CO_2.
- ZIF's have the potential to separate components of biofuels, specifically, water and ethanol.
- ZIF-8 is used to manufacture separation membranes for biofuel applications i.e. alcohol separation.
- ZIF's also have great potential as heterogeneous catalysts; ZIF-8 has been shown to act as good catalysts for the transesterification of vegetable oils.

SYNTHESIS OF ZIF-8 NANOPARTICLES:

Following procedure, for ZIF-8 synthesis was used:

Chemicals Required:

2-Methylimidazole, Methanol, Zinc Nitrate, Ethanol

Procedure:

ZIF-8 crystals were prepared as follows: 2.94g of zinc nitrate ($[ZnNO_3]_{23}[Zn(OH)_2]_3$, Sigma Aldrich) were dissolved in 100ml of methanol (Acros Organics, extra dry, water<50ppm). A solution consisting of 6.56g of 2-methylimidazole (C4H6N2, Aldrich, 99%) and 100ml of methanol was added to the Nitrate based solution and vigorously stirred for 15 minutes. The appearance of the mixture was milky after mixing two solutions. Finally, this solution was centrifugated at 4000 rpm after 24 hours of crystallization time and washed thoroughly with ethanol. Washing of nano-particles was carried out thrice. Then sample was dried at 60^{o}C for 24 hours in oven.

Figure 3: Mixing of reactants

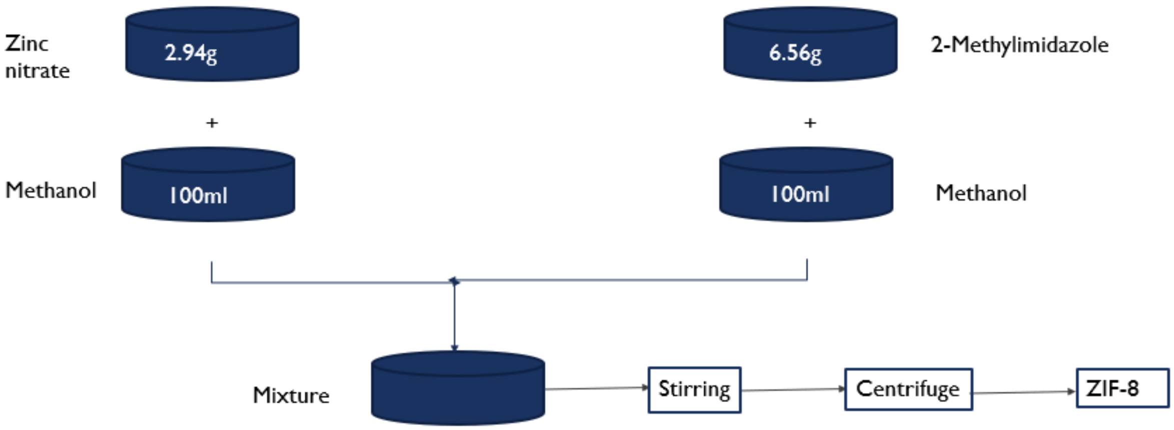

Figure 4: Synthesis procedure for ZIF-8

Yield:

The average yield of one batch was about 800mg of ZIF-8 nanoparticles. It was a white flaky powder after drying in oven. Yield is dependent on synthesis process used and its structure could also be different if different chemicals used in synthesis process.

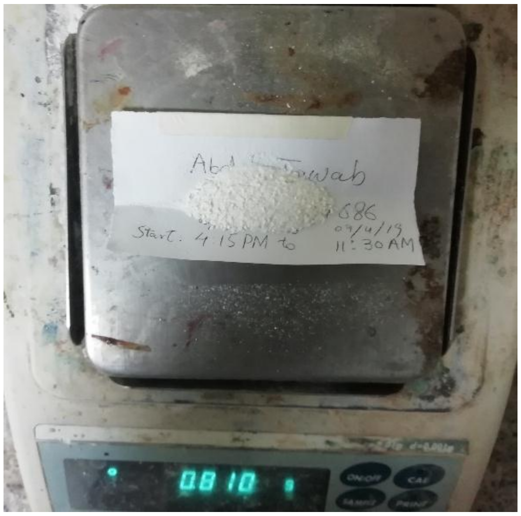

Figure 5: Measurement of ZIF-8 yield

MATERIAL PROPERTIES AND PROPORTIONS:

Cement:

The cement used was 43 grade Bestway cement. Use of different cements can lead to changes in the final strengths of samples so to prevent changing in the results we have used same batch of cement throughout this project. Cement bags were kept in a dry and stable environment to prevent deterioration over time. The measure of a cement samples stability is given by its soundness which was determined to be within reasonable limits. The tests performed on cement are as follows:

Table 5: Properties of cement

Initial setting time	**Final setting time**	**Soundness**	**Specific gravity**	**Bulk density**
ASTM C191	ASTM C191	ASTM C430	ASTM C188	ASTM C188
145 min	270 min	2 mm	3.15	1440 kg/m3

Sand:

Lawrencepur sand was used in mix proportions. Sand servers as a filler in cement matrix and hence it is an important part of the matrix which has implications on the final strength of a mortar sample. Sand can also absorb water which can cause changes in the required water for producing desired workability for preparation of a sample. Tests performed on sand and their results are as follows:

Table 6: Properties of sand

Fineness modulus	**Water absorption**	**Bulk density (oven dried)**	**Specific gravity (oven dried)**
ASTM C136	ASTM C128-07a	ASTM C29	ASTM C128-07a

2.43	1.12%	1466 kg/m3	2.65

Gradation of sand:

Gradation curve of a fine aggregate shows the percentage of a given size of particles in any sample. Due to packing of materials it is important to have a well graded sample i.e. a sample which has all sizes of particles with reasonable proportions. In our case we determined the gradation of sand by using fine sieves and found that the sand sample is in fact well graded so that it can show optimal results.

In our project sand gradation was as follows:

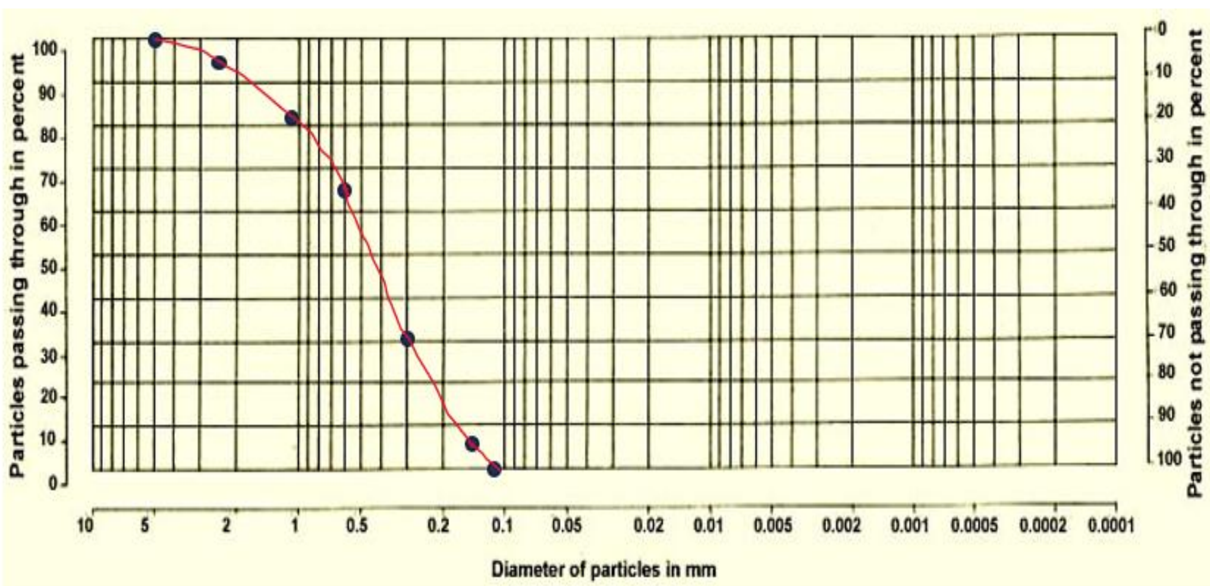

Figure 6: Sand gradation curve

Nano ZIF-8:

Nano ZIF-8 was synthesized in School of Chemical and Materials Engineering (SCME). For characterization of final ZiF-8 yield we performed two tests namely: X-Ray diffraction (XRD) and Scanning electron imaging (SEM). The average grain sizes of the ZIF-8 particles was determined using SEM images.

Crystallite size is the smallest possible crystal size in any given sample which was considerably smaller than average crystal size of the sample. Crystallinity is the percentage of crystals present in a sample while the rest of the sample consists of amorphous solids. Crystallite size and crystallinity of the sample are physical properties of ZIF-8 which were determined for XRD results by first doing appropriate treatment to reduce the noise and uncertainty form the raw XRD results for this we used a dedicated analysis software called High-score (plus). Rest of the properties of ZIF-8 were taken from research papers. Finally, results of ZIF-8 characterization are summarized below:

Table 7: Properties of nano ZIF-8

Crystallite size	**Average grain size**	**Crystallinity %**	**Specific surface area**	**Thermal stability**	**Appearance**
24.9877 nm	100 to 120 nm	76.055%	1200 to 1600 m2/g Source: Kyo Sung Park et. al.	Upto 550C Source: Minqi Zhu et. al.	White powder

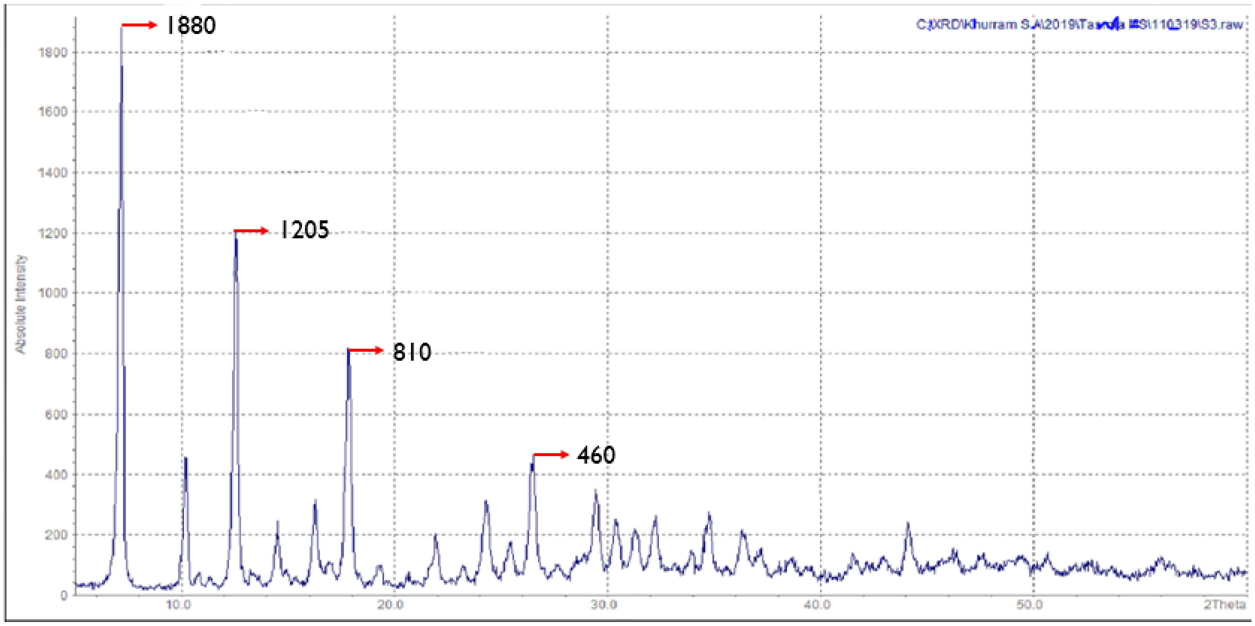

Figure 7: XRD analysis of synthesized sample

Average grain size was determined using SEM analysis of synthesized ZIF-8 and that was about 100 to 120 nm. SEM was performed on three different samples synthesized in lab.

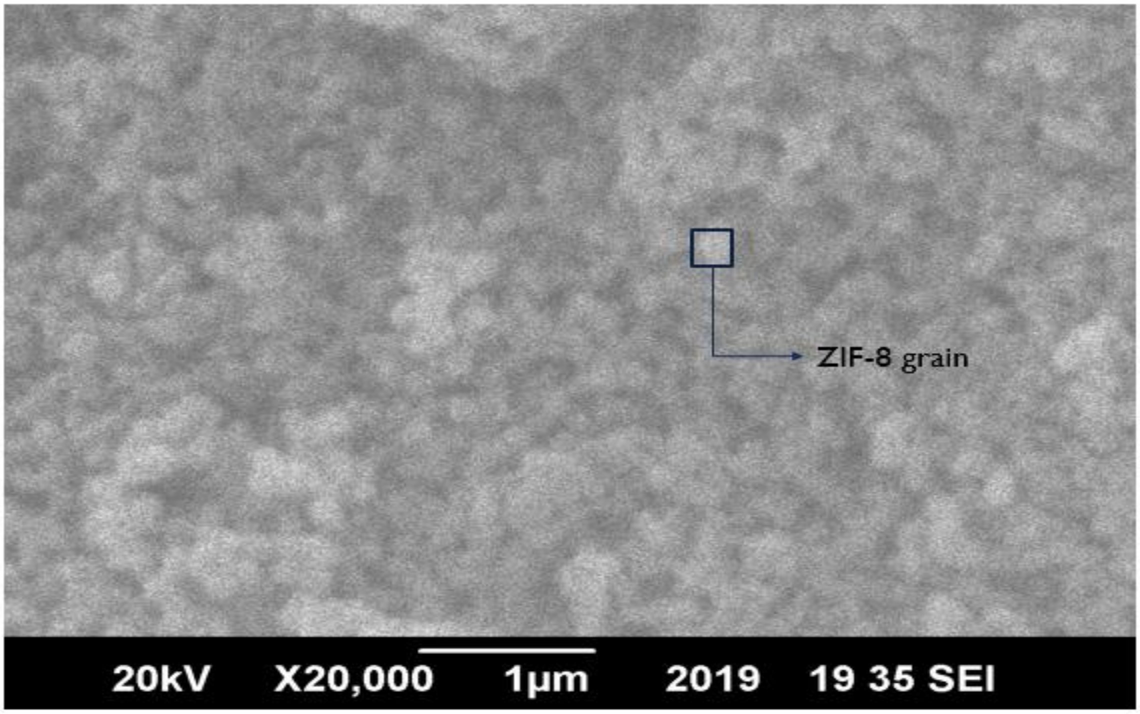

Figure 8: SEM analysis of synthesized ZIF-8

Mix proportions:

A cement mortar mix 1:2 (cement:sand) was used to prepare samples. The control samples were prepared using Lawrencepur sand and Bestway cement and water. Nano ZIF-8 samples were prepared using different percentages of nano ZIF-8 replacing cement. The blends were prepared with cement replacement of 0%, 0.1%, 0.25% and 0.5%. The water cement ratio was 0.35 for all samples.

Dispersion:

Dispersion of Nano-particles involves breaking of agglomerates formed in any media. In our case the medium is aqueous. For adding nano ZIF-8 in to a cement sample we first added it into mixing water for the cement sample but here arises the problem of dispersion. Due to inter-molecular attraction ZIF-8 particles tend to join together in a water sample and form agglomerated particles. This of course is not desired as we want to take advantage of small size of ZIF-8 particles so breaking of these agglomerates is of utmost importance. For dispersion one can use super plasticizer or other chemicals which can retard the ability of particles to agglomerate in any medium. Another method to disperse nano particles is to provide them with acoustic energy so that they may break into smaller sized particles.

To carryout dispersion of nanoparticles bath sonicator was used for 10 to 15 minutes at $30^{o}C$ at frequency of 30kHz. Ultrasound energy from the sonicator broke all agglomerates into dispersed nanoparticles. This was visually confirmed as milky appearance after dispersion.

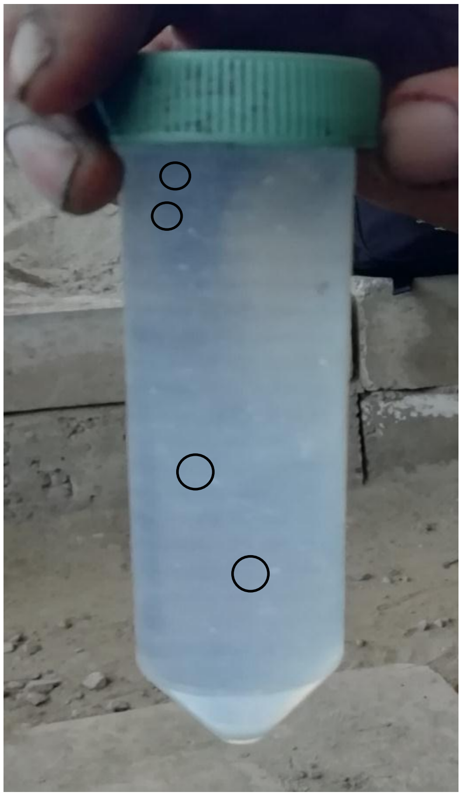

Figure 9: Before dispersion

Figure 10: After dispersion

Testing procedure:

First cement and sand were mixed with a trowel with sand being added progressively. Water was added along with thorough mixing to obtain a cement sand paste. For ZIF-8 samples water with dispersed ZIF-8 was added in cement sand mixture. Hand tamping was used to cast the cubes with 1in layers in 2in x 2in x 2in moulds. Samples were demoulded after 24 hours and placed to cure for 7 and 28 days.

Compressive testing was performed in compressive testing machine according to ASTM C-39. Results obtained are tabulated in results and discussion section.

Study Design:

Different concentrations of ZIF-8 ranging from 0.1-0.5% will be added in cement mortar specimens to determine the optimum range. Percentages of nanoparticles (ZIF-8) were selected depending on specific surface area of ZIFs, as they have a very high specific surface area, so less percentage of ZIFs will be required to fill nano pores in CSH gel. Testing will be done after 7 and 28 days with specimens being kept in water baths for curing. The cement mortar cubes were casted in 50x50x50 mm moulds. Moulds were well oiled before casting. Temperature and humidity conditions were noted for relevant tests. Cement mortar contains 1-part cement and 2-parts sand. Water to cement ratio taken for mixture were 0.35.

Table 8: Study design

Name of group	**Cement %**	**Nano ZIF-8 %**	**Water/cement ratio**	**Cement/sand ratio**
CM0	100%	0%	0.35	1:2
CM0.05	99.95%	0.05%	0.35	1:2
NZ0.1	99.9%	0.1%	0.35	1:2
NZ0.25	99.75%	0.25%	0.35	1:2
NZ0.5	99.5%	0.5%	0.35	1:2

Sample Size:

All compressive strength results are based on three samples of same proportions. For compressive strength three samples of a fixed composition i.e 0.1%, 0.25% and 0.5% of ZIF-8 were replaced in mixtures by weight of cement.

Sample preparation procedure:

Quantities of cement, sand, water and ZIF-8 were weighed and proportioned. First, ZIF-8 was added in water and dispersed for test samples. Hobart mixer was used to prepare cement mortar paste. Paste was placed in well-oiled molds of 50x50x50mm and demolded after 24 hours and placed for curing.

Mix regime (ASTM C305):

Table 9: Mixing regime

Time	**Mixing Regime**
30 sec	Cement was added in water and then sand was added slowly in the mixing bowl at slow speed (139 rpm)
30 sec	Stop mixer, change to medium speed (285 rpm)
90 sec	No mixing interval was given, this time was used to clean the side of the mixing bowl.
60 sec	Finish mixing at medium speed (285 rpm)

RESULTS AND DISCUSSIONS:

Compressive testing Results:

Compressive testing was performed in compressive testing machine and results obtained from testing are tabulated below. These results are average of three samples tested in lab. Maximum seven days strength enhancement was observed upto 42% whereas 28 days strength enhancement was upto 27.55%.

Table 10: Compressive testing results

Sr. No.	Name of group	7-day average strength (MPa)	% Enhancement	28-day average strength (MPa)	% Enhancement
1.	CM0	19.01	-	40.20	-
2.	NZ0.05	22.90	20.46%	43.97	11.05%
3.	NZ0.1	24.30	27.82%	47.46	19.89%
4.	NZ0.25	27.16	42.90%	50.5	27.55%
5.	NZ0.5	23.60	24.14%	45.5	14.92%

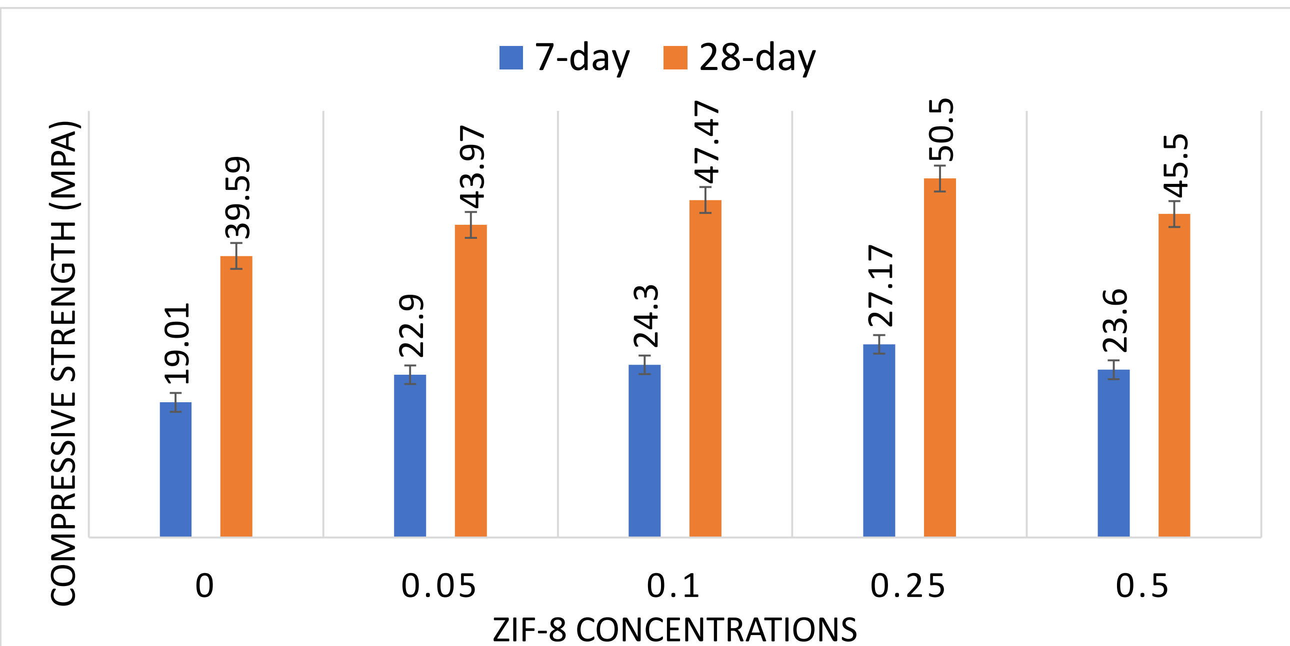

Figure 11: Compressive testing results' comparison

Compared to control all samples showed marked improvement in strength. At 0.05% of replacement of ZIF-8 with cement the enhancement was approximately 20% and 11% for 7 days and 28 days respectively. For 0.1% replacement the enhancement was 28 % and 20 % for 7 days and 28 days respectively. The replacement of 0.25% was determined to be the optimum amount as it showed the maximum average strength enhancement in the samples which are 43% and 28% for 7 days and 28 days respectively. At higher replacement of 0.5%, the strength enhancement was reduced to 24% and 15% for 7 days and 28 days respectively.

Figure 12: Compressive testing on samples

COST ANALYSIS:

To compare the strength enhancement and the prices for this enhancement we developed a rating system. The ratings are given by taking into the account the different prices, optimum contents and strength enhancement of four nano-material strength enhancers so that all of these are compared on a level field.

Market price of nano materials were determined using a single supplier so that changing suppliers may not affect the prices. First of all we assumed that the strength is to be enhanced in a uniform amount of sample which requires a total of 100 g of cement this number is arbitrary and will not affect the final results as we are only drawing a comparison between different nano materials. For a 100 g of cement the optimum amount of respective nano enhancer was determined from sources mentioned in the literature review. The price of the optimum amount for 100 g of replacement was determined. Finally, the total strength enhancement at optimum content was determined from the aforementioned sources and this value was divided by the price of optimum amount for 100 g of cement to give cost for 1% enhancement of the 100g sample at optimum content. It is important to note that this value is only a rating and has no implications in real quantity and cost of any project, but it can, however, be used as a comparison score to determine if any nano material is comparable to others.

In this case the results show that in terms of optimum content, strength enhancement and cost ZIF-8 if not only comparable to the Multiwalled Carbon nanotubes and nano ZnO but also better than nano TiO_2 which is a widely studied nano enhancer.

Table 11: Development of cost rating for different nano materials

Product	**Market price per 100g (PKR)**	**28-day strength enhancement**	**Optimum content (OC)**	**Nano material required per 100g of cement**	**Cost @ OC per 100g of cement (PKR)**	**Cost rating per 1% enhancement**	**Source**
MWCNT’s	21,950	19%	0.5%	0.5g	109.75	**5.78**	Geng Ying Li et. al.
Nano TiO2	8,212	19.3%	0.75%	0.75g	61.59	**3.24**	Salman MM et al.
Nano ZnO	9,628	23%	3%	3g	288.84	**12.56**	D. Nivethitha et al.

Nano ZIF-8	65,292	27.5%	0.25%	0.25g	163.23	**5.93**	-

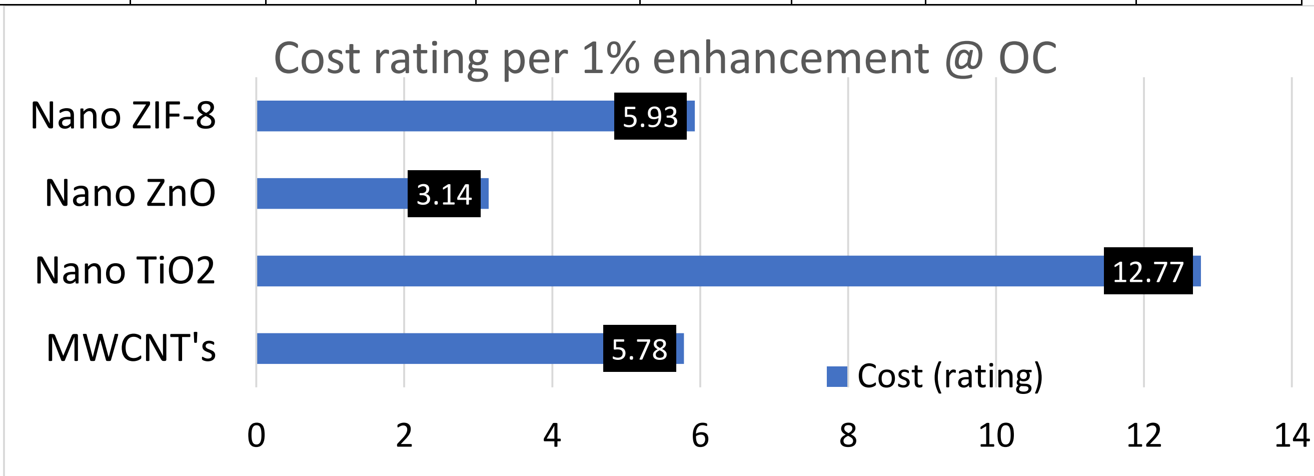

Figure 13: Comparison of cost ratings

CONCLUSIONS:

ZIF-8 can improve upto 27.5% compressive strength for 28-day curing. For 7-day curing, it can improve compressive strength upto 42.9%. The optimum content is about 0.25% of nano ZIF-8 by weight of cement. Cost comparison shows that ZIF-8 can be a feasible nano-material for improvement of mechanical properties of cement mortar. Among all studied nano materials, 28-day strength enhancement by ZIF-8 was maximum.

RECOMMENDATIONS:

- Complete study/analysis should be performed on reinforced concrete in terms of ZIF-8 as an admixture.
- Studies should be performed to determine best dispersion method for ZIF-8 in water.
- ZIF-8 can adsorb high amounts of CO_2, similar studies should be performed on ZIF-8 with adsorbed CO_2.

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