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Microstructure analysis and Strength properties of concrete with Nano SiO_2

B. Kartikeyan, K. Sumanth, G. Harshavardhan, A. Rajasekharareddy and G. Dhinakaran*

School of Civil Engineering SASTRA University, Thanjavur, India – 613402.

***Corres.author: gd@civil.sastra.edu**

Abstract: This study reports part of the experimental investigations on using nano-sized mineral admixtures in concrete as a partial replacement of cement. The silica fume which is the mineral admixture used in this work was ground for 1 hour with varying quantities using planetary ball mill. On analyzing the results of grinding, it was observed that the grinding was effective in 1 hour and the size of micro-silica has reduced by 75.45% reaching nano size. Physical tests such as specific gravity, size identification using particle size analyzer (PSA), micro structure analysis using Scanning Electron Microscope (SEM), Chemical composition identification by X-Ray Fluorescent (XRF), Crystalline check for silica using X-Ray Diffraction (XRF) were performed for samples of both unground and ground micro-silica (nano silica). Mechanical properties were obtained by performing strength tests for specimens cast with different percentages of ground and unground micro-silica in partial replacements such as 5%, 10% and 15% by weight of cement. From the results it is understood that cubes cast with 10% replacement of nano silica for cement by weight are showing better strength performance.
Key words: nano sized mineral admixtures, Micro-silica, PSA, SEM, XRD, XRF, Strength.

Introduction

To reduce the environmental pollution created by cement industries, the usage of cement must be limited which automatically controls the manufacture of cement. Supplementary cementitious materials are those which are added to concrete as a part of the total cementitious system to reduce the total quantity of cement to be used and most significantly to increase the strength of concrete from its normal to high strength. Micro-silica, Fly ash, ground granulated blast-furnace slag, calcined clay, metakaolin, and calcined shale, supplementary cementitious materials which contribute to the strength gain of concrete.

Pozzolans usually increase the mechanical strength and durability of concrete structures there by playing an important role when added to Portland cement. They impart strength by bringing changes in microstructure of the cementitious paste and in the pore structure by the reduction in the grain size caused by the pozzolanic reactions pozzolanic effect (PE) and the reduction of pores and voids by the action of the finer grains [1]. Mineral admixtures such as Micro-silica, Rice hush Ash, Fly ash, bagasse ash [2] which are rich in pozzolanic actions and fillers such as lime stone fillers [3] can be used as a partial replacement for cement in high strength concrete. Many works were performed and are still in progress regarding the usage of these mineral admixtures in High Strength Concrete (HSC) and High Performance Concrete (HPC). The long term strength of concrete obtained using these mineral admixtures will be more, the short term strength of concrete can be increased by 1) Increasing the fineness of the mineral admixtures 2) Curing at elevated temperatures 3) Using chemical activators [4].

Finer particles are being used in construction industry in recent years. Several works were performed on use of nano particles in concrete specimens as mineral admixtures to improve physical and mechanical properties [5]. Most of the works were done using readily available SiO_2 nano particles [6-11]. Some works were also performed using nano Al_2O_3[12], nano Fe_2O_3[13] and Zinc-iron oxide nano particles[14] as mineral admixtures in concrete. Also the use of nano sized mineral admixtures were also studied on self compacting concrete using SiO_2 [15, 16], Fe_2O_3[17] and ZnO_2[18,19].

In addition the effects of several types of nano particles on properties of concrete specimens which are cured in different curing media were investigated in several works [19]. It is observed from the literatures that the use of nano particles in concrete improves the mechanical properties of the specimen in addition to the improvement in microstructure of the concrete specimen. From the above literatures it is found that most of the researches were done using a small amount of nano sized mineral admixtures as an additive in a small amount in concrete.

Many research works are being done for obtaining high strength or high performance concrete using mineral admixtures, Zhu. W et al [20] presented a state-of-art report on application of nano technology in the field of construction. In that a summary about the background of nanotechnology, examples of nanotechnology-enabled materials that are available in markets were provided. Quanlin Niu et al [21] analyzed the effect of superfine slag powder and found that use of superfine slag powder increased the packing properties of cement paste and in addition to that, the porosity and pore size distribution of the pastes were also improved and due to the more complete hydration of the superfine slag section, the strength of the mortars also increased. Guangcheng Long et al [22] studied the effects of compound paste systems containing ultrafine powders such as pulverized fly ash, pulverized granulated blast furnace slag and micro-silica, a very-high-performance concrete was prepared using large quantities of ultrafine powders which offered a compressive strength up to 200 MPa. Pacheco-Torgal et al [23] discussed about attaining High Performance Concrete using nano particles. The paper summarized the knowledge of using nano particles in concrete and the benefits in using them such as improving mechanical properties of HPC, controlling calcium leaching by efficient dispersion of nano particles etc.

Significance of the present research work

Though use of nano particles as a partial replacement for cement play a major role in increasing the compressive strength of concrete, improving microstructure and pore structure of concrete specimen the cost of manufacturing nano sized particles is very high which limits their use liberally. In the present work it has been tried to improve mechanical properties of HSC prepared using locally available mineral admixtures in nano-size or ultra-fine size. The aim of this study is to obtain nano sized mineral admixtures economically using conventional methods such as ball milling and investigating the strength and durability characteristics of specimen cast with nano sized mineral admixtures as a partial replacement for Ordinary Portland Cement.

Experimental investigations

Material properties

The physical characteristics of various materials used in this work are reported as shown below.

Cement

The cement used was ordinary Portland cement of grade 53 having a specific gravity of 3.16. The chemical composition of the cement is presented in Table 1.

Table 1: Physical properties of cement

S. No.	Material	Specific gravity
1.	Cement	3.15
2.	Fine aggregate	2.63
3.	Coarse aggregate	2.55
4	Ungrounded Silica fume	2.20
5	Ground Silica fume	2.40

Mineral admixtures

The mineral admixture used in the present work is micro-silica which is a by-product obtained from Ferro silicon industries. For the present project work Micro-silica is obtained from Oriental Exporters, Navi Mumbai, Maharashtra. The particle size of unground micro-silica was analyzed using PSA and it was found to be 0.638µm. The chemical composition of the micro-silica was found using XRF and it is presented in Table 2.

Table 2: Chemical composition of silica fume obtained by XRF

Formula	Concentration (%)
SiO_2	97.36
MgO	0.79
Al_2O_3	0.53
SO_3	0.51
K_2O	0.29
Fe_2O_3	0.15
CaO	0.14
P_2O_5	0.09
Na_2O	0.06
Cl	0.02
MnO	0.01
PbO	0.01
TiO_2	0.01
Cr_2O_3	100 ppm
ZnO	70 ppm
CuO	51 ppm
Ru	47 ppm

Aggregate

River sand was used as fine aggregate and the fineness modulus of the fine aggregate is 3.17 and it belongs to coarse sand category which can be used for concrete mixing. The specific gravity of the fine aggregate was noted as 2.63. Aggregate passing through 16 mm sieve and retained on 12.5 mm sieve was used as coarse aggregate in the concrete mixture. The specific gravity of the coarse aggregate was noted as 2.65. The fineness modulus of the coarse aggregate is obtained as 7.5.

Super plasticizer

A commonly available super plasticizer CONPLAST SP 430 from FOSROC Company was used through this project to obtain the workable concrete mix.

Water-cement ratio

The water cement ratio was kept between 0.31 and 0.33, as the percentage of micro-silica increased; the requirement of water required also increased.

Concrete mixture proportions

In the present work a high strength concrete grade of M50 has been adopted, ACI method has been adopted to arrive the mix design. A total of 7 combinations were prepared for the present research work control, UGSF5, UGSF10, UGSF15, GSF5, GSF10, and GSF15. The combinations were made by partially replacing cement with ground and unground micro-silica in 5%, 10%, 15%. The obtained mix ratio is 1:1.04:2.13 (Cement: Fine aggregate: Coarse aggregate). The mix proportion details are shown in Table 3.

Specimen details

The specimens were cast as per BS 1881. Concrete cubes of size 100 mm x 100 mm x 100 mm and cylinders of size 100mm x 200 mm were cast to study the compressive and tensile strengths. Strength tests of cube and cylinder specimens were performed in automatic compression testing machine with a capacity 3000 kN. Specimens were subjected to stress controlled loading.

The specimens were prepared by partially replacing cement in the concrete mix in 5%, 10%, 15% of unground micro-silica (UGSF) and ground micro-silica (GSF), in addition, control concrete specimens were also cast in which no partial replacement was done.

Table 3: Mix proportioning

S. No	Parameters	Mix Properties
1.	Grade of concrete	M50
2.	Mix Proportion	1:1.04:2.13
3.	Cement (kg/m^3)	522.57 kg/m^3
4.	Fine Aggregate (kg/m^3)	544.18 kg/m^3
5.	Coarse Aggregate	1113.84 kg/m^3
6.	Water	182.9 l/m^3
7.	Super plasticizer	1-3(*l*) per 100 kg of cement

Results and Discussion:

General

The variations of compressive strength of specimens for different combinations of mix proportions are discussed in the following paragraphs.

Effect of grinding

The grinding efficiency of the mill depends upon several parameters such as the amount of materials to be ground, the ratio of the material to the grinding balls and the size of the grinding balls. Fig.1 shows the planetary ball mill of 320 r.p.m. used for grinding micro-silica. 10 mm zirconium balls were used in grinding process. Initially 18 balls were added and after twenty minutes the numbers of balls were increased to 26. Initially 100 g of micro-silica was fed into the ball mill the sample was ground for 1 hour, later 50 g of micro silica was ground for one hour to study the effect of grinding and the details are presented in Table 4. It was found that 100g micro-silica ground for one hour showed reduction in size by 20.84 % compared to the unground micro-silica, but a reduction of 75.45 % was observed when the quantity was reduced to 50g maintaining the same grinding time. The nano size is achieved in 1 hour grinding when 100g of micro-silica is fed in the planetory ball mill and when the quantity was reduced to 50g for the same 1 hour duration the size was reduced considerable and showed a size of 156.6 nm,this may be due to the micro-silica particles are coming into contact in a larger amount with the zirconium balls and grinding becomes more effective. Figures 2, 3 and 4 show the PSA results of UGSF and micro-silica ground for 1 hour in varying quantities. Table 4 shows the percentage of reduction obtained.As the nano size is achieved in 1 hour grinding, the optimum duration of grinding is fixed as 1 hour.

Fig.1 Ball mill

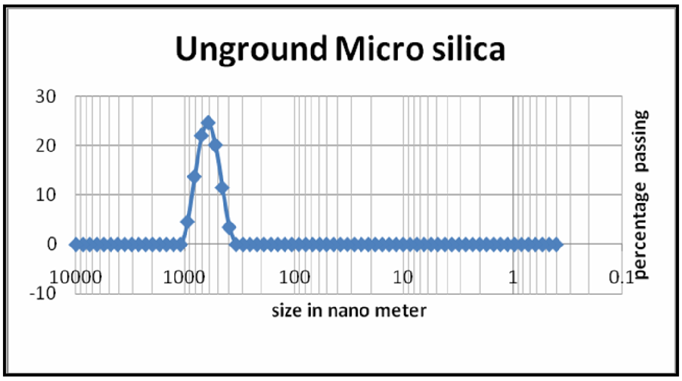

Fig.2. PSA results of unground micro silica

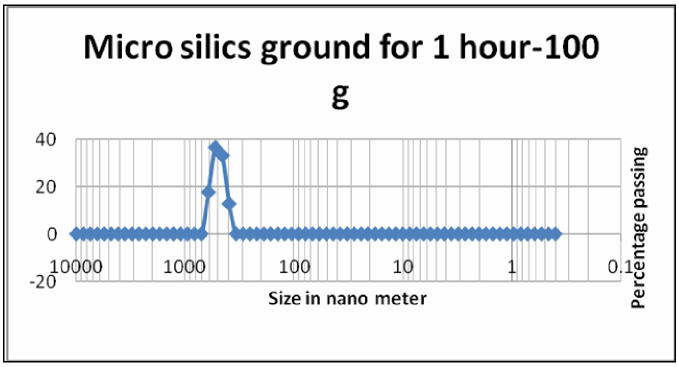

Fig.3. PSA results of 100 g micro silica ground for 1 hour

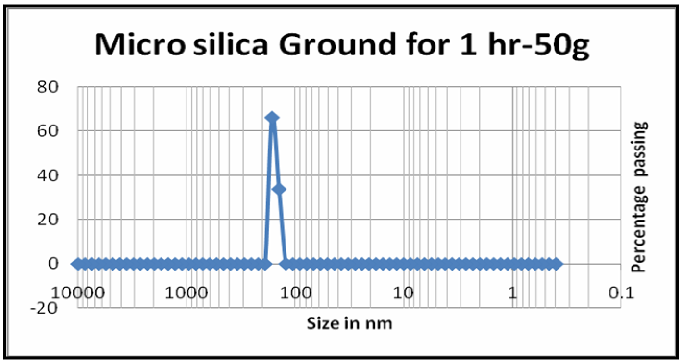

Fig.4. PSA results of 50 g micro silica ground for 1 hour

Table 4: Size of ground and ungrounded silica fume

Sl.No	Sample Type	Quantity used for Grinding (g)	Duration of Grinding	Size	Percentage reduction in size
1	UGSF	-	-	0.638μm	-
2	GSF	100	1	0.505μm	20.84
3	GSF	50	1	156.6 nm	75.45

Effect of GSF and UGSF in Compressive strength

The variation of compressive strength of concrete with different percentages of micro-silica after subjecting to 28 days curing is shown in Fig.8. From the results it is observed that the compressive strength of conventional concrete is 54.67 N/mm^2 which more than the characteristic compressive strength 50N/mm^2. Hence it is ensured that the quality control during preparation of concrete is up to the desired standard. On analyzing the 28 day strength results of cubes cast with UGSF it is observed that the strength of the cubes decrease by 14.79 percentage when replaced in 15%, cubes cast with 10 % replacement of UGSF showed an increase in strength by 3.56 percentage and those cast with 5% replacement of GSF showed a decrease in strength by 10.48 %. In a similar way on comparing the strength of cubes cast with GSF it was observed that there was an increase in strength by 0.5% and 7.4% for cubes cast with 5% and 10% of GSF partially replaced with cement and a decrease in strength by 7.5 % was seen for cubes cast with GSF partially replaced by 15% for cement. The short term strength of cubes when replaced with supplementary cementitious materials will be less initially when compared with the control concrete cubes, but the long term strength will be more. So it is under stood that partial replacement of 10% of GSF can give better strength compared to all other combinations. The state of cubes when subjected to testing and after reaching the maximum compressive strength is shown in Fig.5 and Fig.6.

Effect of GSF and UGSF in split tensile strength

The average tensile strengths of control concrete mix and concrete replaced with unground micro-silica and micro-silica ground for 1 hour using planetary ball mill by 5, 10 and 15 percentages were shown in Fig 9. On analyzing the results it was observed that the cylinders cast with 10% and 15% replacement with UGSF showed an increase in tensile strength by 8 % and 2.4% whereas cylinders cast with 5% UGSF showed a decrease in strength by 41.33% and those cast with 5% GSF showed a decrease in strength by 24% only, which means that the decreasing in strength percentage has reduced due to the packing of nano sized silica particles. The strength of cylinders cast with 10 % and15% increase by 19.2 and 12 percentages compared with the controlled concrete specimen. From the results it is understood that cylinders cast with nano sized silica show better results compared with cylinders cast with unground micro-silica among them cylinders cast with 10% GSF showed better results. The state of the cylinder after reaching the maximum tensile strength is shown in Fig.7.

Fig.5 Cube being tested

Fig. 6 Crushed state of cube

Fig.7 State of cylinder after applying tensile load

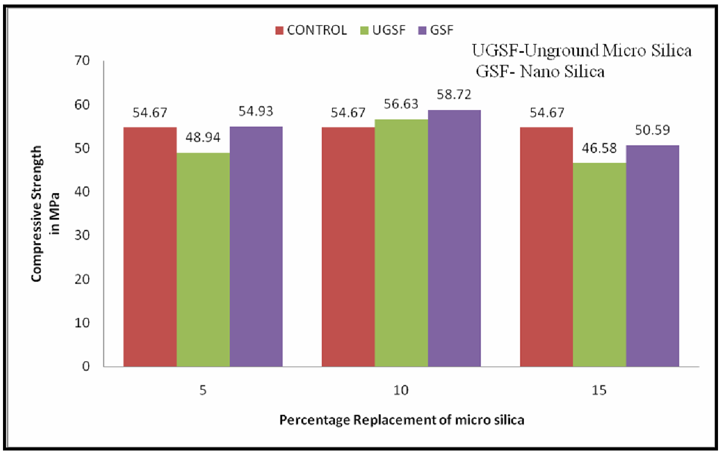

Fig.8 28 days Compressive strength comparison between UGSF and GSF

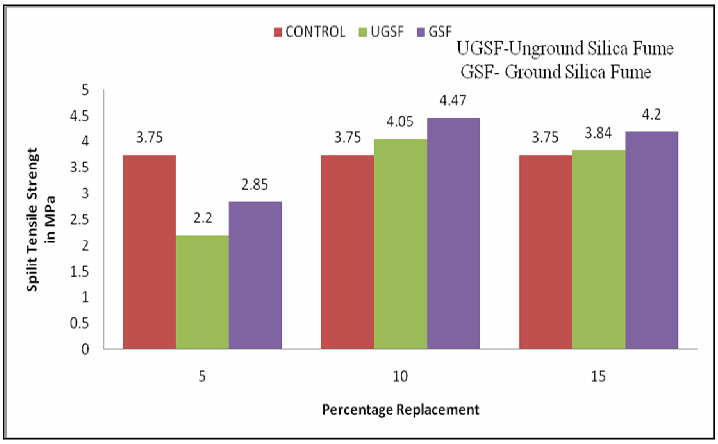

Fig.9 28 day Tensile Strength comparisons between UGSF and GSF

Scanning Electron Microscope (SEM) Observation of micro structure:

The micro structure of unground micro silica and micro-silica ground for 1 hour by varying the input quantity as analysed by Scanning Electron Microscope were shown in figures 10, 11, 12. The sizes of the ground and un ground samples can also be seen. From the SEM images it is understood that there is considerable reduction in size for the same grinding hours by changing the quantity to be fed in the mill. Also on observing the images it can be seen that the micro structure of the ground particles were not disturbed compared with the unground sample. When it is subjected to long periods of grinding the spherical shape of the particles may even get reduced but in our project we have stopped with 1 hour grinding considering the economy.

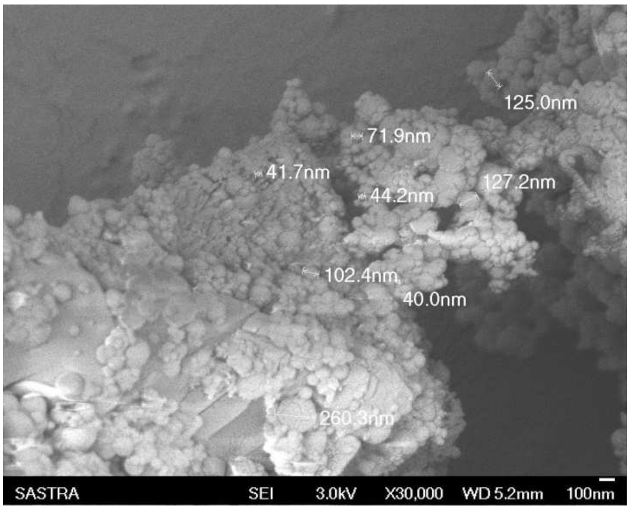

Fig.10 Morphology of Unground Micro Silica

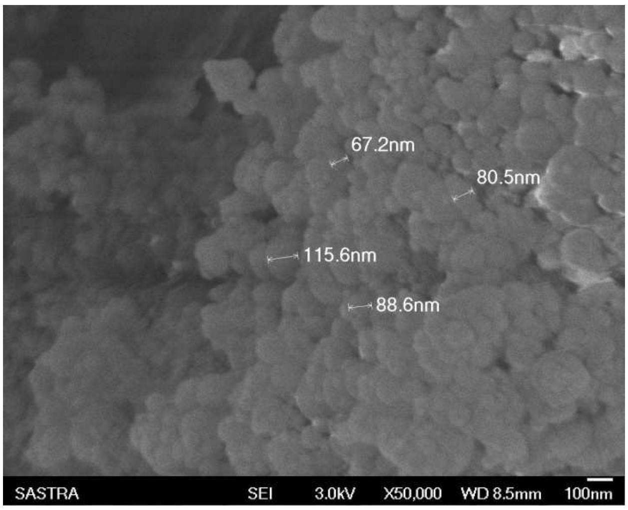

Fig. 11 Morphology of 100 g micro silica ground for 1 Hour

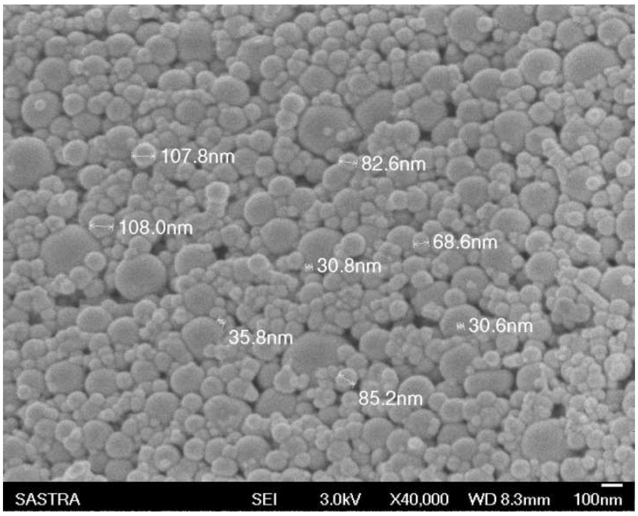

Fig. 12 Morphology of 50 g micro silica ground for 1 hour

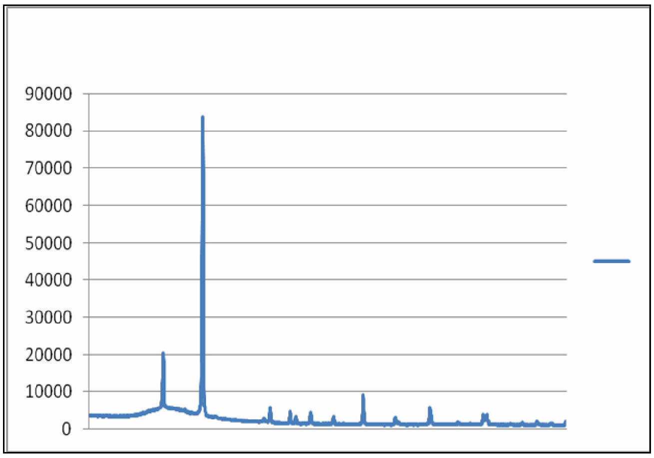

Fig. 13 XRD pattern of unground silica fume

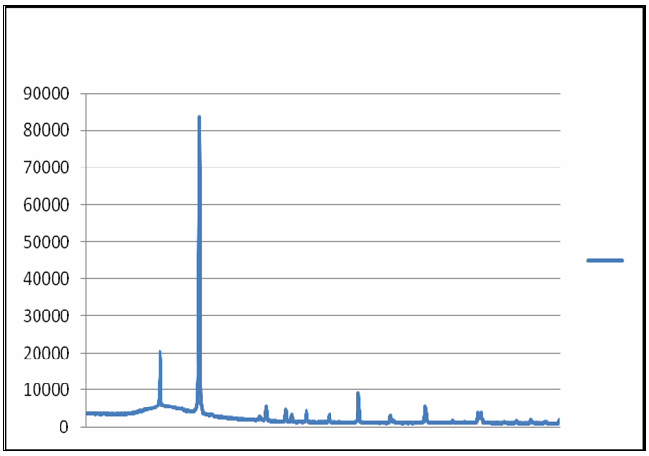

Fig. 14 XRD pattern for silica fume ground for 1 hour

XRD pattern of UGSF and GSF

The XRD pattern for unground micro-silica and micro-silica ground for 1 hour is shown in Fig.13 and Fig.14. It is observed from XRD the nature of SiO_2 is crystalline. The crystalline nature of the un ground micro-silica and nano sized silica remain same and is not affected due to grinding.

Conclusions

Experimental investigations were carried out on normal strength concrete added with GSF to understand the effect of replacing ultrafine particles on strength and permeability characteristics. From the experiments conducted, following conclusions were arrived:

The results from Particle size analyzer shows the effect due to grinding and it is observed that that size of the micro-silica particles got reduced from 0.638 µm to 156.6 nm when subjected to different hours of grinding with varying quantities of micro-silica.

On observing the morphology of the micro-silica it is noted that the sizes of the micro-silica were not affected due to grinding.

The optimum grinding period is fixed as 1 hour as the nano size was achieved when micro-silica is ground for one hour.

The XRD pattern of micro-silica before and after grinding for one hour remains same.

The increase in strength achieved in 28 days is almost equal to the control concrete specimens because specimens cast with partially replaced mineral admixtures show better strength only when subjected to long term curing, anyhow here we are able to achieve the strength nearer to control concrete strength and more strength can be achieved when subjected to curing for longer periods.

The compressive strength of the concrete cubes cast with partial replacement of ground micro-silica (GSF) for cement in 10 percentages showed an increase by 7.5% compared with control concrete cubes.

The split tensile of concrete cylinders cast with 10 % GSF an improved strength of 19.2 % compared with cylinders cast with control concrete cylinders.

On comparing the overall compressive and tensile strength of the concrete specimens, the specimens cast by replacing micro-silica in 10 % provided an overall increase in strength for both ground and unground cases.

Abbrevations

SEM :	Scanning Electron Microscope
PSA:	Particle Size Analyzer
XRD :	X-ray Diffraction
XRF:	X-Ray Fluoroscent
SF:	Silica Fume
GSF :	Ground Silica Fume
GSF5 :	Specimen with 5% ground micro silica
GSF10 :	Specimen with 10% ground micro silica
GSF15 :	Specimen with 15% ground micro silica
UGSF:	Unground micro silica
UGSF5:	Specimen with 5% Unground micro silica
UGSF10 :	Specimen with 10%Unground micro silica
UGSF15 :	Specimen with 15% Unground micro silica

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