Effect of Size and Dosage of Mineral Admixtures: Microsilica and Nanosilica on Compressive Strength withMicrostructureAnalysis of Concrete

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Abstract: In the present investigations microsilica and nanosilica are used as mineral admixtures, with particlesizesin the range 0-20 µm, 20-45µm, 45-90 µm,90-125 µm and 125-250µm and the dosages adopted in the investigations are 0% to 40%, with an increment of 10% for compressive strength,cubes were casted and tested. In the first phase compressive strength (optimum) is found, which is obtained at 20% replacement level for 0-20µm particle size.In second phase by considering 20% replacement as optimum value obtained for microsilicaasreference and varying the percentage of nanosilica from 2% to 6% with an increment of 2%, again the cubes were casted and tested, the optimum compressive strength is observed at 4% nanosilica and 20% microsilica replacement. The microstructural analysis is carried out using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).The elements analysed in the study before and after the pozzolinc reactions are silica and calcium, their consumptions in terms of percentage are obtained using energy dispersive spectrometer.

Keywords: microsilica, nanosilica, scanning electron microscopy, energy dispersive spectroscopy.

I.INTRODUCTION

The ever progressive civilizationand social advancement have been significantly influenced by the application of concrete and steel in establishing infrastructural facilities. The global consumption of concrete is next only to waterand hence concrete rightfully enjoys the unique position as the most widely used construction material.The major concerns associated with the cement production are environmental and sustainability issues and intense energy needs. The production of cement releases approximately an equal amount of CO_2 into the atmosphere due to the calcinations of limestone and combustion of fuel.

Microsilica is a by-product obtained by the smelting process in the silicon and ferrosilicon industry. .Microsilica is also identified as silica fume, condensed silica fume, volatilized silica or silica dust. Microsilica has been recognized as a pozzolanic admixture that is effective in improving the mechanical properties to a great extent. By using microsilica along with super-plasticizers, it is comparatively easier to obtain higher compressive strength.

Nanotechnology has attracted considerable scientific interest due to the new potential uses of particles in nanometer (10^{-9}m) scale. The nano scale size of particles can result in dramatically improved properties from conventional grain size materials of the same chemical composition.

The term microstructure indicates the structure which develops in concrete at a micro level, when water is added to cement and aggregates. To understand the cause, extent and mechanism of deterioration, or how to improve some of the properties of concrete, a thorough awareness of the basic microstructure of hardened concrete is required .Mechanical properties of concrete more often depend on its intrinsic microstructure. The high resolution capability of SEM coupled with EDS/EDXA has opened a world of opportunities in the field of concrete technology. The microstructure of concrete is described as an integrated system consisting of (i) hydrated cement paste (ii)coarse and fine aggregates and (iii) the interface between aggregate and hydrated cement paste, also known as interfacial transition zone (ITZ). The SEM has two modes of operation that are of prime importance

1) It has the ability to produce images with surface details in the range of 1-5 nm with sufficient depth of field to give three dimensional effects.

2) Secondly it can be utilized for electron beam production of x rays which facilitates in analysis of volumes as small as 1µm in diameter.

There are two types of images produced using SEM namely back scattered electron (BSE) images and secondary electron (SE) images which provide imaging facility. Both BSE and SE image modes provides imaging facility, never the less, BSE is more oriented for detecting atomic density which can be related to the atomic number and density of grains forming the object. It is known that material having higher atomic number shows higher reflection. In cement, the C_4AF phase is brighter due to the existence of iron whose atomic number is 26 compared to calcium and aluminum in C_3A phase, however that SE mode is more focused and is used for the topographic contrast. The most significant limitations of any microscopic technique is that increased magnification reduces the sampling area and therefore sample representation decreases

SantanuBhanja and BratishSengupta [1] investigated the strength of silica fume concrete at a constant water binder ratio (w/b) of 0.34 and replacement percentages varies from 0 to 25. The maximum 28 day compressive strength was obtained at 15% replacement level. They also studied the silica fume effect with different water binder ratios. In their study it is observed that the maximum strength was obtained at 25% replacement of cement by silica fume. Duvel and Kadri [2], studied the workability and the compressive strength of silica fume concretes for low water-cementations materials ratios with super plasticizer. They observed optimum compressive strength at 20%replacements and the strength gain is less than 15%.Swami et al. [3] have investigated, effect on strength and chemical resistance of concrete for M25 grade by using microsilica 920-D. The percentage of microsilica used in the investigation is ranging from 0% to 40%. The optimum strength is obtained at 10% replacement. Benturet.al.,[4] reported that the strength of silica fume concrete is greater than that of silica fume paste which they attributed to the change in the role of the aggregate in concrete. Mazloom et.al.[5] investigated the influence of silica fume on the compressive strength of high performance concrete. Wild et.al [6] stated the difference in strength development in OPC concrete and silica fume concrete. Sobolev [7] studied the compressive strength of high performance concrete. Wong and Razak [8] studied the compressive strength of concrete containing silica fume and w/c ratio kept as variable factor. Behnood and Ziari [9] designed the concrete mixtures to evaluate the effect of silica fume on the compressive strength. Koksal et.al [10] investigated the compressive strength of hooked ends steel fiber concrete with silica fume.Mohammad Bolhassani and MohammadrezaSamani [11], nanosilica in powder and colloidal form and their effect were investigated with specific surface area of particles varying from 80m^2/gm to 380m^2/gm, on the mechanical properties including workability on cement paste and mortar. The use of nanosilica enhanced the strength of cement paste, compared to the control mix. However, by increasing the specific surface area more than 90m^2/gm, the compressive strength of specimens decreased.Vagelis G. Papadakis [12] proposed a theoretical modelling and evaluated an expression to find the consumption of calcium hydroxide with silicafume in concrete.Byung-Wan jo et.al [13] compressive strength of cement mortar was investigated with silicafume and nanosilica for different w/c ratios and dosages, it is observed that compressive strength was higher for cubes with nanosilica addition. G.Quercia et.al [14] presented the application of nanosilica in concrete, their manufacturing process and effect. They concluded that, the use of nanosilica in concrete reduces CO_2 foot print and also increases the properties of concrete. RafatSiddique et.al [15] reviewed the physical, chemical properties, reaction mechanism, hydration characteristics, workability and compressive strength of cement paste and mortars. G Land et.al [16] nanosilica particles of different sizes and specific surface area were synthesized, XRD showed that the consumption of C_3S and $Ca(OH)_2$ were accelerated by addition of silicafume.Rajamane N.P et.al [17] investigated silicafume addition to cement mortar mix along with nanosilica(colloidal form), causes considerable increase in strength and reduction in water permeability.G. AppaRao [18] investigated the addition of silicafume on compressive strength for different water cement ratios and dosages. Sidney Diamond et.al [19] analysed particle sizes and their dispersion in concrete of densifiedsilicafume.

From the above studies, it is observed that there were no investigations noticed with the range of particles and various replacements for microsilica and nanosilica. In this paper the effect of both were presented in detail, with the evidence of experimental study.

II. EXPERIMENTAL PROGRAMME

In the experimental programme, to evaluate the compressive strength, the particle sizes in the range 0-20 µm, 20-45µm, 45-90 µm,90-125 µm and 125-250µm were used and the dosages adopted in the investigations are 0% to 40%, with an increment of 10% , cubes were casted and tested.The microsilica replacement is at 10% to 40% with an increment of 10%, whereas for nanosilica it is 2%, 4% and 6%.The results are presented in the discussions of test results. In addition to test results, the microstructure of concrete is also analyzed.The grade concrete used is M20, cubes cast were of size 150mmx150mmx150mm with mix proportion of 1:2.65:4.55 and W/C ratio of 0.5. The superplasticizer used is CONPLAST-SP 430.

III.MATERIALS

The following materials were used in the experimental investigations

Cement: Thecement used in the investigations is ordinary Portland cement (OPC) of 53 grade. Physical and chemical properties are presented in table 1 and 2.

Table 1Physical Properties of Cement

Specific gravity	Bulk density (kg/m^3)	Surface area(m^2/kg)
3.09	1865	340

Table 2 Chemical Properties of Cement

Cao	Sio_2	Al_2o_3	Fe_2o_3	Mgo	So_3	P_2o_5	K_2o	Na_2o	Tio_2
60.84	16.34	6.95	5.38	2.32	1.99	1.67	2.73	1.50	0.28

Fine aggregate: River sand is used as fine aggregate, which is of grade II, based on particle size distribution. The properties are tabulated in table 3.

Sl no	Description	River sand
1	Specific gravity	2.64
2	Bulk density(loose)kg/m^3	1480

Table 3 Physical Properties of River Sand

3	Bulk density(compacted)kg/m^3	1695
4	Fineness modulus	2.45
5	Grading zone	II

Coarse aggregate: Crushed granite stone is used as coarse aggregate in the investigation.

Super Plasticizer: The super plasticizer used in the present work is CONPLAST-SP430 in the form of Sulphonated Naphthalene polymers complies with IS: 9103-1999, to improve the workability of concrete.

Water: Locally available portable water is used for mixing and curing of the specimens.

Microsilica: Microsilica 920-D is used in this experimental programme, which is supplied by ELKEM INDUSTRIES MUMBAI and the properties are tabulated in table 4 and 5.

Table 4 Physical Properties of MicrosilicaTable 5**Chemical** Properties of Microsilica

Particulars	Microsilica
Specific gravity	2.27
Surface area m^2/kg	20000
Particlesizemicrometer	<1
Bulk density kg/m^3	187.91
Loss on ignition (%)	1.92
PH	7.90

Sl no	Chemical component	%by weight
1	Sio2 (%)	85-95
2	Sio3 (%)	0.18
3	Cl (%)	0.12
4	Total alkali (%)	0.66
5	Moisture content (%)	0.16
6	Loss of ignition (%)	1.92
7	PH	7.90

Nanosilica: Nanosilica used in the experimental investigations is supplied by SISCO RESEARCH LABORATERIES MUMBAI, the properties are tabulated in table number6 and 7.

Table 6Physical Properties of NanosilicaTable 7Chemical Properties of Nanosilica

Particulars	Nanosilica
Specific gravity	2.2-2.5
Surface area m^2/gm	210
Particle size in nm	5-14
Bulk density kg/m^3	-
Loss on ignition (%)	0.67
PH	4.1

Sl no	Chemical component	% by weight
1	Sio_2	99.97
2	Sio_3	-
3	Cl	-
4	Total alkali	-
5	Moisture content	-
6	Loss of ignition	0.67
7	PH	4.1

V. RESULTS AND DISCUSSIONS

The compressive strength for various replacements and particle sizes with and without nanosilica are presented in the table IXtoXV. From the table, it is observed that the compressive strength increases as the particle size decreases which are observed at 7, 14, 21 and 28 days of testing of samples. At 28 days of testing, the percentage increase at 10%, 20%, 30% and 40% replacements for 0- 20µm, when compared with 125-250µm particle size, it is equal to 28%, 28%, 26% and 19% respectively. The increase in compressive strength is more at 10% and 20% replacement of cement by microsilica and it decreases at 30% and 40% replacements. The optimum strength is obtained at 20% replacement level, the percentage increase in strength, when compared with control mix for 0-20µm particle size is 42%.

At 20% replacement, the compressive strength is optimum, by considering it as the reference and varying the percentage of nanosilica at 2%, 4% and 6%, the optimum compressive strength is obtained at 4%NS and 20%MS replacements. The percentage increase, when compared with control mix is for above said combination for 0-20µm particle size is 67% and that for 125-250µm particle size it is equal to 20%. The percentage increase when compared between 125-250µm particle sizeand 0-20µm particle sizes, it is equal to 38%.

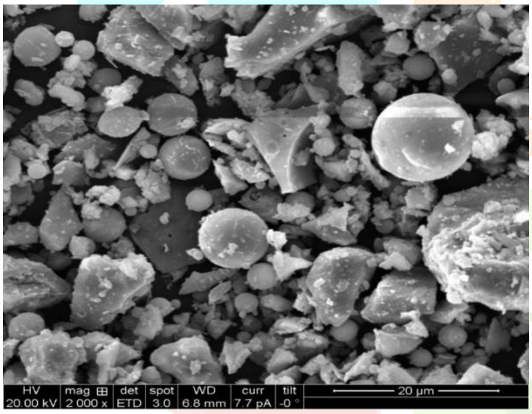
The tables are shown for 20% replacement of microsilica , and combination of 4% nanosilica and 20% microsilica replacement, along with SEM and EDS/EDXA (optimum strength) for above said combinations.

For example the SEM image for cement(figure 1) shows the particles are spherical and non-spherical in morphology at 20 kv,2000 magnification , at working distance of 6.8 mm .The EDS/EDXA for cement(figure 2) shows the various elements and oxides present as percentage weight or atomic percentage weight. The silica present is 17.62% and calcium is 53.60% by weight (tableVIII). By considering these two elements as reference, the investigations is carried out to know the physical mechanism and chemical mechanism involved in the pore structures of concrete and pozzolanic reactions that take place after addition of mineral admixtures. When mineral admixtures are added as percentage replacement for cement, the percentage weight of silica and calcium consumed and remained unreacted can be calculated.The percentage weight of silica and calcium present in cement, microsilica, nanosilica are shown in the SEM and EDS/EDXA.In the SEM micrograph the following compounds can be identified

	Wt%	**At %**	**K-Ratio**	**Z**	**A**	**F**
O K	9.99	19.98	0.0152	1.0716	0.1421	1.0003
MgK	0.47	0.61	0.0029	1.0231	0.5939	1.0055
AlK	6.86	8.13	0.0497	0.9948	0.7218	1.0084
SiK	17.62	20.08	0.1408	1.0251	0.7749	------
S K	3.40	3.39	0.0290	1.0108	0.8301	1.0155
K K	1.55	1.26	0.0151	0.9681	0.9432	1.0736
CaK	53.60	42.79	0.5095	0.9891	0.9596	1.0016
FeK	6.52	3.74	0.0564	0.8942	0.9669	1.0000
Total	100.00	100.00				

1. ETTRINGITE---pipe like structures without branches of size 4-5µm in length.
2. CALCIUM HYDROXIDE OR PORTLANDITE----hexagonal structures.
3. C-S-H ---fibrous type to irregular grains forming a reticular network (cotton shaped like structures).

Table 8 EDS FOR CEMENT



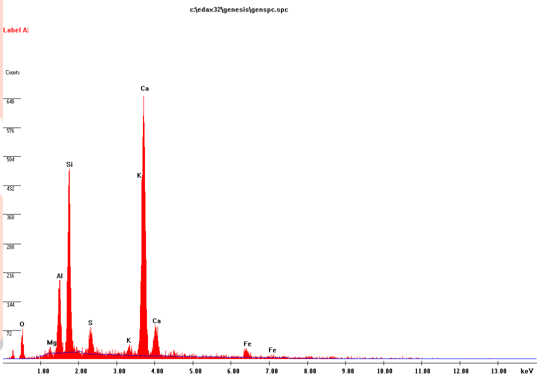
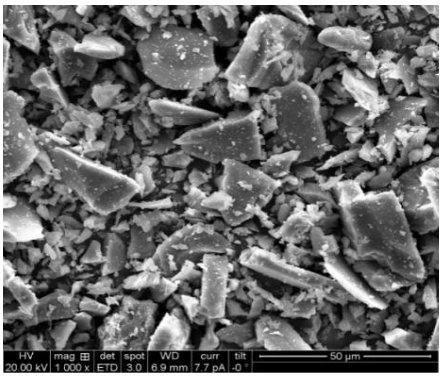
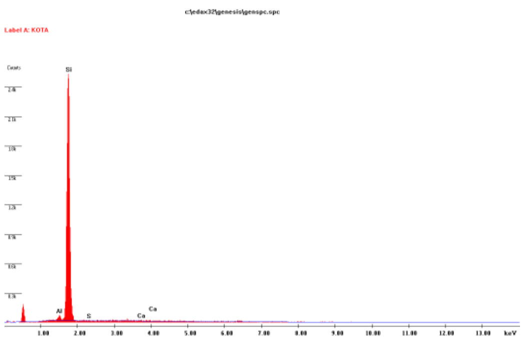


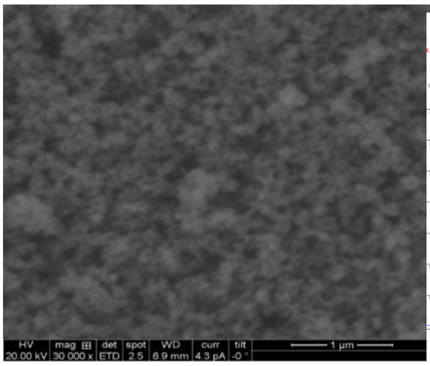
Fig.1: SEM Diagram for Cement **Fig.2:**EDS for Cement

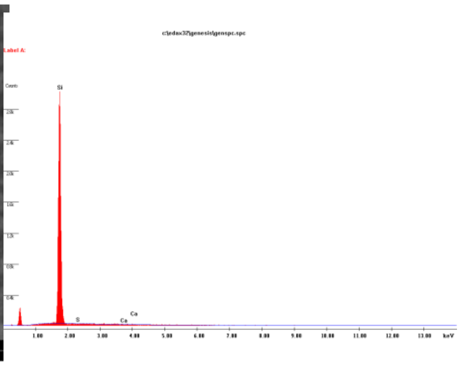




Silica present as per EDS is 83.89% by weight

Fig.3:SEM Diagram for Microsilica**Fig.4:**EDS for Microsilica





Silica present as per EDS in nanosilica is 99.71%

Fig.5: SEM DIAGRAM FOR NANOSILICA**Fig.6:** EDS FOR NANOSILICA

Table 9 Compressive strength at 10% replacement of cement by micro silica

Sl.No	**Particle Size(μm)**	**Compressive Strength(Mpa)**			
		7 days	**14 days**	**21 days**	**28 days**
Compressive strength for control mix		14.65	18.40	21.75	25.90
1	0-20	17.80	22.20	31.20	34.50
2	20-45	16.50	20.40	28.70	32.50
3	45-90	15.60	19.20	27.10	30.60
4	90-125	15.10	18.60	25.90	29.30
5	125-250	14.70	17.70	23.80	26.90

Table 10Compressive strength at 20% replacement of cement by micro silica

Sl.No	**Particle Size(μm)**	**Compressive Strength(Mpa)**			
		7 days	**14 days**	**21 days**	**28 days**
Compressive strength for control mix		14.65	18.40	21.75	25.90
1	0-20	20.1	23.6	35	36.9
2	20-45	17.8	21.5	31.5	34.4
3	45-90	16.5	19.8	29.1	31.6
4	90-125	15.8	19.4	27.4	30.3
5	125-250	15.3	18.2	26.1	28.7

Table 11Compressive strength at 30% replacement of cement by micro silica

Sl.No	**Particle Size(μm)**	**Compressive Strength(Mpa)**			
		7 days	**14 days**	**21 days**	**28 days**
Compressive strength for control mix		14.65	18.40	21.75	25.90
1	0-20	19.80	23.10	34.60	36.70
2	20-45	17.20	21.10	31.20	34.10
3	45-90	16.10	19.40	28.40	31.20
4	90-125	15.40	18.90	27.10	29.80
5	125-250	15.10	17.70	25.60	28.30

Table 12Compressive strength at 40% replacement of cement by micro silica

Sl.No	**Particle Size(μm)**	**Compressive Strength(Mpa)**			
		7 days	**14 days**	**21 days**	**28 days**
Compressive strength for control mix		14.65	18.40	21.75	25.90
1	0-20	17.00	21.30	26.80	28.90
2	20-45	16.40	19.80	25.40	27.20
3	45-90	15.40	18.60	23.90	25.70
4	90-125	15.10	17.90	23.30	25.20
5	125-250	14.10	17.30	22.40	24.20

Table 13Compressive strength on replacement of 2% NS and 20% MS

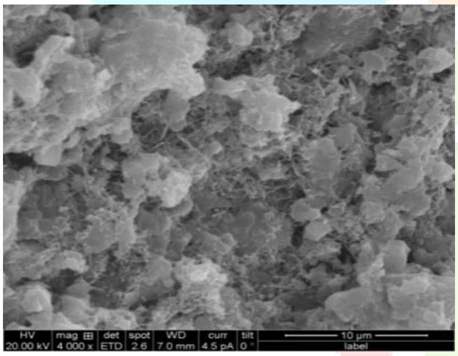
Sl.No	Particle Size(µm)	Compressive Strength(Mpa)			
		7 days	14 days	21 days	28 days
Compressive strength for control mix		14.65	18.40	21.75	25.90
1	0-20	23.80	31.30	37.20	40.20
2	20-45	21.40	27.50	34.50	37.30
3	45-90	18.80	24.10	31.80	34.80
4	90-125	17.50	22.70	30.00	32.10
5	125-250	16.10	19.90	27.40	30.20

Table XIV: Compressive strength on replacement of 4% NS and 20% MS

Sl.No	Particle Size(µm)	Compressive Strength(Mpa)			
		7 days	14 days	21 days	28 days
Compressive strength for control mix		14.65	18.40	21.75	25.90
1	0-20	25.90	35.20	39.80	43.30
2	20-45	23.80	30.10	37.10	40.20
3	45-90	21.40	26.70	33.50	36.80
4	90-125	19.60	24.20	31.40	34.20
5	125-250	18.60	22.10	29.20	31.30

Table 14:Compressive strength on replacement of 6% NS and 20% MS

Sl.No	Particle Size(µm)	Compressive Strength(Mpa)			
		7 days	14 days	21 days	28 days
Compressive strength for control mix		14.65	18.40	21.75	25.90
1	0-20	24.20	31.50	37.50	42.90
2	20-45	21.50	27.50	35.10	40.00
3	45-90	19.50	24.40	31.30	35.80
4	90-125	18.50	22.60	28.70	33.00
5	125-250	17.30	20.30	26.40	30.20



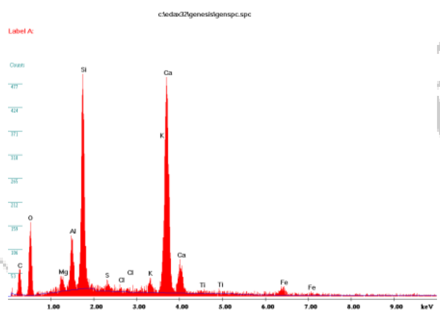
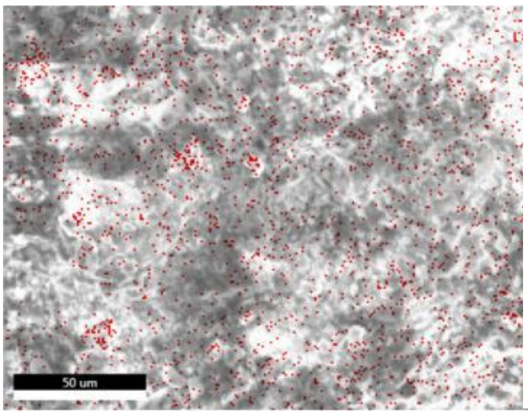


Fig.7: SEM image at 20% replacement**Fig.8:** EDS at 20% replacement of cement

The percentage weight of silica and calcium after reactions found to be equal to 17.22% and 37.38% from the EDS table.



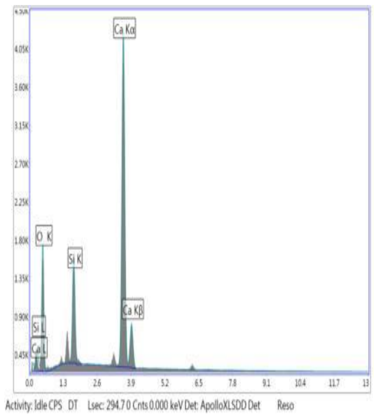


Fig 9 and 10: SEM image and EDS at replacement of 4% NS and 20% MS

VI. CONCLUSIONS

From the experimental investigations conducted on microsilica and nanosilica , the following conclusions were drawn

1. As the particle size decreases, the strength increases .The strength depends upon the specific surface area of the mineral admixtures used in the investigations.
2. The specific surface area for cement is 340m^2/kg, microsilica 20000m^2/kg and for nanosilica it is 210m^2/gm. Since the specific surface area for nanosilica is more, when compared to microsilica, so more space available for the pozzolanic reaction to take placeHence addition of nanosilica along with microsilica gives more strength.
3. The optimum compressive strength is obtained at 20% replacement of cement by microsilica. For 0-20µm particle size, strength is maximum, the reason could be smaller size particles, more specific surface area available for pozzolanic reaction to take place and hence more strength.It is observed that for 0-20µm particle size, the compressive strength is 36.9 MPa, the percentage increase when compared with control mix is 43%, whereas for 125-250µm particle size the increase is 10%.
4. The SEM micrograph for 20% replacement clearly shows the formation of C-S-H gel, portlandite with ettringite also in the concrete matrix. The SEM image is dense and compact when compared with other replacements.From EDS table, the quantity of silica and calcium consumed in the pozzolanic reaction is equal to 13.65gm and 5.5gm, since more quantity of silica is consumed in the pozzolanic reaction, hence more strength.
5. The compressive strength is optimum for 4%NS+20%MS replacements , and the maximum strength is obtained for 0- 20 µmparticle size, which is equal to 43.3 MPa .The percentage increase when compared with control mix for 0-20 µm is 67% and that for 125-250µm is 21%. The higher strength is due to nanosilica presence in concrete mix, where in the particle size is in nanometer, which fills the capillary pores of cement more effectively, also due to high specific surface area, their pozzolanic reactivity will be high in the cement hydration, and hence the concrete is more dense and compact, if they are dispersed properly.
6. The SEM image shows the matrix, which appears dense and compact when compared to other replacement level. The EDS table confirms the quantity of silica and calcium consumed in the concrete mix is equal to 23.19gm and 13.29gm, which is confirmed by the peaks.
7. Comparing the strength of samples of other dosages and even different range of particle sizes, have shown moderately lesser strength at 28 days period when compared with 20% replacement of micro silica of 0-20µm size particles. The reason could be higher particle sizes from 125-250µmto 90-45µm used for reaction, which have lesser specific surface area and also the filling of capillary pores in cement is less because of higher particle sizes.

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