EFFECT OF ELEVATED TEMPERATURES ON THE PROPERTIES OF NANO ALUMINA MODIFIED CONCRETE CONTAINING ZIRCON SAND AS FINE AGGREGATE

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This paper reports the experimental investigations conducted to assess the behaviour of nano-alumina modified concrete containing zircon sand as fine aggregate at varying proportions of 5%, 10%, 15%, 20% and 25% by weight. To evaluate the combined effects of nano-alumina and zircon sand the mechanical and durability properties of concrete at ambient and at elevated temperatures the concrete mixes were tested after subjected to various temperatures of 200^{0}C, 400^{0}C, 600^{0}C, and 800^{0}C. The specimens after cooling were tested for compressive strength, flexural strength, ultrasonic pulse velocity, water absorption and porosity evaluation. The analysis of test results showed that the inclusion of nano-silica and zircon sand in concrete has increased the residual strength of the concrete at all heating regimes. Finally the SEM and XRD studies were conducted on the modified concrete to examine the micro-structural and chemical composition changes in the concrete due to temperature elevation.

Keywords: *Nano alumina, temperature elevation, zircon sand, mechanical properties, microstructure*

1. Introduction

Concretes must sustain extreme conditions especially when used in public structure and buildings [1]. Fire is one of the serious threats to the buildings and may cause severe hazards to public safety and human life [2]. Fire resistance is one of the essential parameter that a concrete must contain in addition to strength and durability [3]. The change in the chemical and physical changes of concrete after exposure to temperature may weaken the chemical bond leading to structural collapse and undesirable failure of structures [4]. The choosing of appropriate materials is therefore necessary to eliminate the devastating effects caused by the concrete structures especially when they are exposable to high temperatures such in furnaces or reactors [5]. The concretes in the power reactors and furnaces may almost reach a temperature upto 1300^{0}C which may lead to the loss of the bonding capacity [6] thus creating extreme spalling and explosive blasting [7]. Hence a concrete is said to be qualifying construction material only when they are able to sustain extreme weather conditions and high temperatures [8].

Several studies have investigated the temperature effects on the strength and durability of concrete [9-11]. The effects of additions of pozzolanic admixtures and supplementary cementitious materials on the temperature stability of concrete were also critically examined [12]. Some studies have also tried to analyse the effect of micro and nano materials on the properties of concrete after exposure to elevated temperatures [13]. Nano materials have been used to improve the specific properties of concrete at ambient and elevated temperatures and have yielded positive results due to emerging of nano-technology as a technological weapon [14]. The concrete structures when subjected to high temperatures may lead to the rise of internal pores (micro and meso) due to internal dehydration. Nano materials due to their high temperature stability and filling capacity may fill the pores thereby reducing the concrete disintegration and internal structure degeneration by delaying the failure occurrence. Studies relating the property evaluation of concretes by adding nano materials are numerous. Only a handful of studies have been done on the utilization of nano-alumina in concrete at normal and elevated temperatures. The nano alumina materials as additives have also increased the mechanical and physical properties of concrete after exposure to higher temperatures due to their pore shifting characteristics [15].

Earlier research works have reported that the use of nano particles in concrete restricts the pores in the interfacial transition zone of the aggregate and the cement paste. The degree of reduction of pores depends on the fraction of nano particle and the type of aggregate usage. The zircon sand is essentially a new concept to the world of concrete construction. However their thermal stability and fracture resistance is a well established concept. Insufficient studies to clearly demonstrate the effect of use of zircon sand in concrete forms the basis of

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the present research work. The study sets out to study the combined effect of nano alumina and zircon sand on the properties of concrete at ambient and elevated temperatures. The possibilities of utilizing the thermal stability of zircon sand to enhance the thermal behavior of concrete is to be analyzed when nano alumina are also added as a cement replacement. The novelty of the present research work lies on the analysis of combined effect of nano-alumina and zircon sand on the thermal stability concrete. Zircon sand is mainly used in ceramic industry to withstand high temperatures. No studies have been done utilizing zircon sand as concrete ingredient as per our knowledge. The residual mechanical strength and UPV were analyzed after exposure to higher temperatures. The microstructure of the temperature exposed nano silica modified zircon sand concrete is also analyzed by SEM and XRD studies.

2. Materials

Ordinary Portland cement in compliance to 12269-1987 is used as cement binder, 2% nano alumina (by weight of cement) was added as binder additive. Zircon sand and natural river sand was used as fine aggregate. Both conformed to Zone II as per BIS 383-1970. The highly pure analytical grade nano alumina was purchased from Astra Chemicals, India. The physical and chemical properties of the nano alumina and zircon sand are shown in Table 1. Zircon sand was supplied by the Essar & Co, India. Water to cement ratio was fixed at 0.48 and superplasticizer dosage was maintained constant at 0.75% throughout the mixes. The target slump achieved was 70 cm for the control concrete. The gradation curves of the materials used in concrete manufacture is shown in Fig 1. The chemical composition of the starting materials are tabulated in Table 1 obtained by XRF technique. The X-ray Fluorescence spectrometer XGT-5200, Horiba was used to analyze the elemental composition of the raw materials. The samples were initially dried to constant weight and about 15 g of the powder samples were poured in its loose state into the sample cup for the measurement.

Zircon sand may also contain some radioactive impurities and hence the measurement of radioactivity becomes essential when used in building components. The zircon sand used in the present study showed an effective dosage value of 0.4 mSV (as per manufacturer's datasheet) which is within 1 msv. Hence the use of zircon sand can be used in building material since the dosage limit for radiation is not a breach. The purity of nano-alumina was confirmed through XRD and TEM studies as shown in Fig 2 and 3.

Table 1

Chemical composition of the cement, sand and zircon sand

Component	OPC (%)	S (%)	ZS (%)
SiO_2	41.447	99.27	-
Al_2O_3	-	-	7.311
Fe_2O_3	2.490	-	4.155
CaO	53.781	-	-
V_2O_5	-	-	0.384
Cr_2O_3	-	-	0.465
ZrO_2	-	-	87.685
K_2O	1.087	-	-
TiO_2	1.195	-	-
GeO_2	-	0.721	-
TeO_2	-	0.009	-

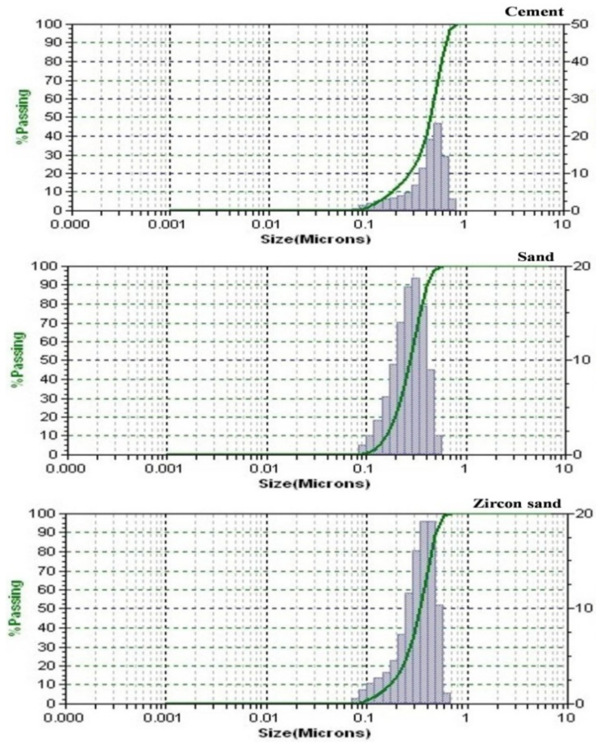

Fig 1- Particle size distribution of materials used in concrete.

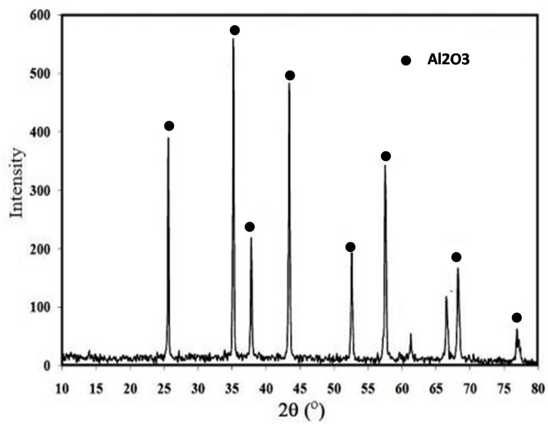

Fig 2 - XRD Analysis of Al_2O_3 Nanoparticles.

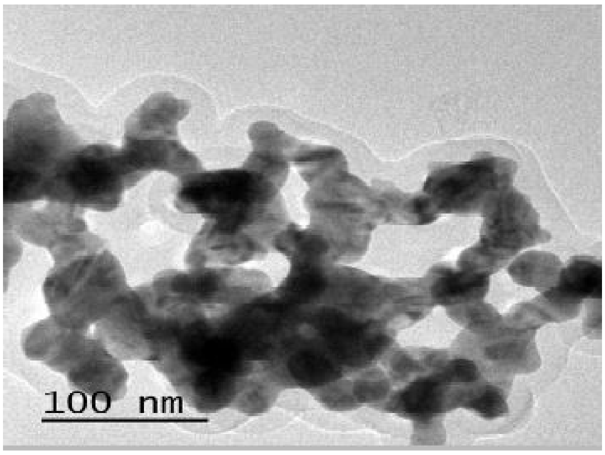

Fig 3 - TEM Analysis of Al_2O_3 nanoparticles.

3. Methodology

Six different concrete mixes containing varying proportions of zircon sand were produced as shown in Table 2. The dispersion of nano-alumina in concrete is the major factor that determines the strength of nano modified concretes. To ensure the proper dispersion of nano materials in concrete superplasticizer is used as a dispersing agent in concrete. Initially the nano particles were mixed with superplasticizers and then added to the concrete so that uniform dispersion is attained.

The fresh state property of the concrete mixes was analyzed through ensuring the slump values. The concrete cubes were cast of size 150 x 150 x 150 mm to measure the compressive strength using digital compression testing machine of 200 ton capacity. The beams of 100 x 100 x 500 mm dimension were cast to obtain the flexural strength of the concrete mixes using Flexural Testing machine of capacity 100 kN. The ultrasonic pulse velocities were measured on concrete cubes of size 100 x 100 x 100 mm as per IS 13311-1(1992) through longitudinal measurement of the time of transit using ultrasonic tester (CONTROLS). The water absorption tests were conducted on circular discs of 100 mm diameter and 50 mm thickness. The fragments of the specimens before and after subjected to high temperatures were sealed in plastic bags to carry out the microscopic studies. The fragments were sized 3-4 cm after drying in oven at around 60^0C. The scanning electron microscopy studies were done to understand the morphological changes. The crystalline phases present in the mortar were identified through the patterns obtained from X-ray diffractometer (Xpert Pro, PANalytical) that uses using Cu K_a radiation with λ= 1.54 Å.and the patterns were recorded at ^{0}2 theta angle (2Ɵ) ranging from 10 to 80^0. The SEM images were obtained from SEM, ZEISS EVO device operating at secondary electron mode at an accelerating voltage of 40 kV. The EDAX analysis was also performed to analyse the chemical elements present in the mixes through line analysis methodology.

After curing of the concrete specimens at 28 days, the concrete specimens were then subjected to elevated temperatures of 200^0C, 400^0C, 600^0C and 800^0C starting from the room temperature. The electric furnace after reaching the temperature was maintained at the same temperature for about 2 hours to ensure uniform heating of the specimens. After then the samples were allowed to cool naturally to reach the room temperature after which the testing is done. The property of the concrete at each temperature was then compared to the concrete properties at normal temperature. Three samples were cast for each mix and the test values were reported as the average of the three specimens for each experimental test.

4.Results and discussions

4.1 Slump

The workability of the concrete modified using nano alumina as a function of increasing zircon sand substitution is shown in Fig 4. The results clearly confirmed the variation in the slump of the concrete with varying zircon sand proportions due to their glassy structure. Moreover the inclusion nano particles reduce the workability of concrete due to their high water demanding capacity to wet their high surface area. The results comply to the previously obtained results which shows a negative influence on the workability due to nano particle substitution in concrete. However the present study showed improvement in the workability due to the zircon sand substitution that compensated the loss in workability caused by

Table 2

Concrete compositions and proportion of replacements

MIX ID	w/b ratio	BINDER		FINE AGGREGATE		COARSE AGGREGATE
		CEMENT	NANO-ALUMINA	SAND	ZIRCON SAND	
		%	%	%	%	%
CM	0.48	100	0	100	0	100
CZ1	0.48	98	2	90	5	100
CZ2	0.48	98	2	80	10	100
CZ3	0.48	98	2	70	15	100
CZ4	0.48	98	2	60	20	100
CZ5	0.48	98	2	50	25	100

nano alumina. The slump results comparable to that of the normal concrete were obtained as significant result of zircon sand substitution.

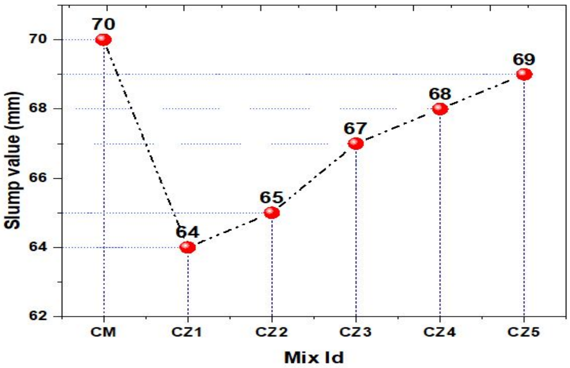

Fig. 4 - Slump values of various concrete mixes.

4.2 Compressive strength

The residual compressive strength of the concrete mixes after subjected to high temperatures in comparison to the strength at normal temperature is shown in Fig 5. Nano-alumina addition increased the strength of the concrete at all temperatures. The improvement in the strength may be due to the filler effect exhibited by the nano-alumina. Essentially the properties of the concrete depend on the filer efficiency and hence the compressive strength increment is an effect of the super fine nano-alumina that filled the pores in the concrete and also strengthened the interfacial transition zones of the concrete. Zircon sand substitution may prove to be inefficient in improving the strength of concrete at normal temperatures but at higher temperatures the contribution of zircon sand is noteworthy. The angularity and temperature stability of zircon sand may reduce the soundness of the concrete after exposure to high temperatures which reduces the spalling of the concrete. Moreover the interlocking behavior of the nano-alumina with the zircon sand has yielded the improved compressive strength. The higher particle packing capacity of the varying sizes of nano alumina, zircon sand and fine aggregates have contributed to the improved residual compressive strength.

4.3 Flexural strength

The measured flexural strength of the concrete mixes is shown in Fig 6. It can be seen that the inclusion of nano-alumina increased the flexural strength of the concrete. The pores in the concrete affect the flexural strength of the concrete especially causing failure at the interfacial zone. The water around the fine aggregates may also be clogged inside the pores thereby forming a weak transition zone around the aggregates leading to failure of the specimens. The zircon sand fine aggregates function as reinforcing agents as well as filling agents due to their strength characteristics and gradation characteristics. The nano-alumina on the other hand is a better nucleating agent that forms dense CSH gels by promoting the consumption of CH. This enhanced formation of CSH gels also well surrounded the fine aggregates thus improving the denser and compact concrete structure. The strength loss was minimized at all the temperatures at increasing zircon sand substitution which indicates the effect of nano-alumina that increased the hydration of cement matrix thereby reducing the slipping planes.

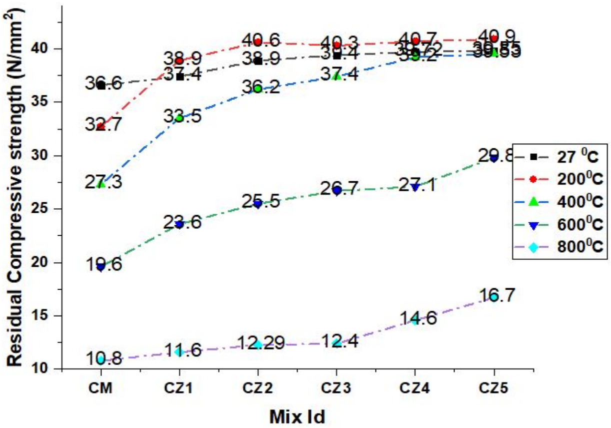

Fig. 5 - Residual compressive strength of the concrete mixes at different temperature.

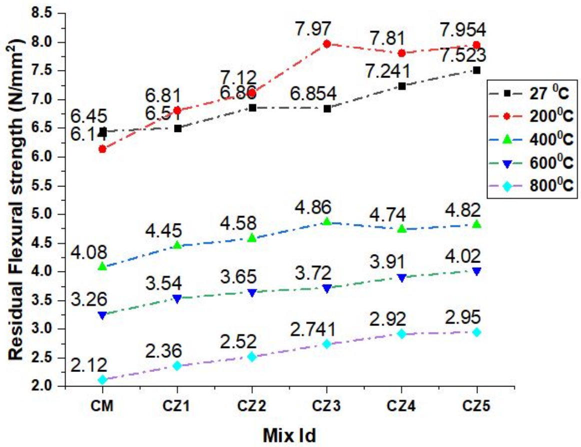

Fig 6 - Residual flexural strength of the concrete mixes at different temperature.

4.4 Porosity

The porosity of the concrete mixes at normal and elevated temperatures is shown in Fig 7. The nano-alumina dosage has caused a significant reduction in the porosity of the concrete mixes at normal temperatures. This reduction in porosity is not only an influence of nano-alumina but also a result of zircon sand substitution. No concrete mixes exhibited increased porosity at any temperatures when compared to the normal concrete which confirms the impermeable

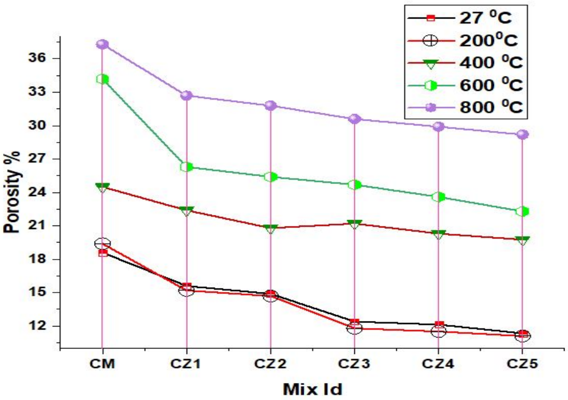

Fig. 7 - Porosity of the concrete mixes at different temperature

behaviour of the produced concrete mixes. The reason of the reduced porosity may be the combined effect of pore filling capacity of zircon sand and nano-alumina. The formation of CSH from the $Ca(OH)_2$ may lead to the increase pores in the cement matrix after subjected to elevated temperatures. No significant reduction in porosity values of the concrete mixes much different from the control concrete due to the presence of nano-alumina that absorbed more water due to their higher surface area. This physically absorbed water when heated may get lost thereby increasing the porosity. The zircon sand compensated the negative effects caused by the nano-alumina because the zircon sand generally absorbs less or negligible water when compared to the conventional fine aggregate and hence the water deteriorations in concrete is usually minimized.

4.5 UPV

The ultrasonic pulse velocities of the concrete mixes at normal and elevated temperature are shown in Fig 8. A significant improvement in the ultrasonic pulse velocity was observed in the concrete mixes was observed in the concrete mixes at normal temperature. The Ultrasonic Pulse Velocity depends mainly on the compactness and denseness of the concrete. More number of pores leads to the deviation in the ultrasound and hence taking more time to reach. The increase in the handling time automatically decreases the UPV values. It has already been established in several research works that there exists an inverse relationship between UPV and porosity of the concrete mixes. The pulse velocity of concrete decrease with increase in voids present in concrete. The higher ultrasound velocities indicate that the concrete is good in terms of density, uniformity and pore structure quality.

The gradual decrease in the ultrasound velocities of the concrete was also observed in the concrete mixes up to 600°C. This confirms the higher thermal stability of the zircon sand to hold up their properties even at high temperatures. The reduction in ultrasonic pulse velocity is due to the.

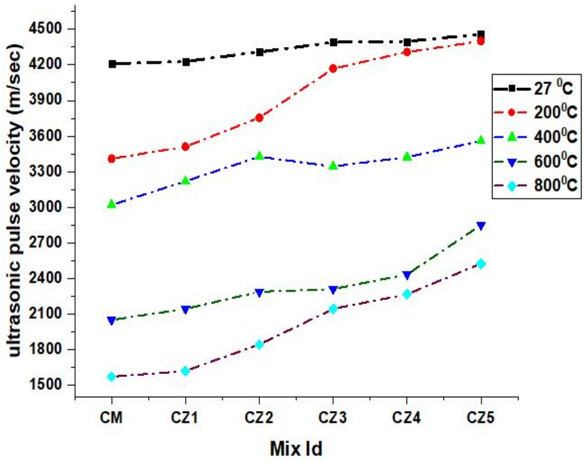

Fig 8 - Ultrasonic pulse velocity of the concrete mixes at different temperature

increase in the pore structure and micro cracking of the concrete after exposure to higher temperatures. The residual ultrasonic pulse velocity varied significantly with respect to that of the control concrete due to the interlocking behaviour exhibited by the zircon sand and nano-alumina. Almost all the mixes of concrete belonged to ‘good’ concrete quality grading upto 400°C as per the quality gradation given in IS 13311-1 (1992). Another reason for such an improved ultrasonic pulse velocity may also be due to increased formation of CSH that possess the self healing capacity to fill the pores formed due to heating of the concrete.

4.6 Regression analysis

The regression analysis performed from the experimental results and model that fits the experimental parameters of the concrete at normal and elevated temperatures is obtained . The prediction equation obtained from the regression analysis and the corresponding R^2 value obtained are shown Fig 9. The higher R^2 value obtained were and shows that the strength parameters of the concrete are inter-related to each other at normal temperatures which validates the experimental results.

4.7 XRD

The X-ray diffraction of the concrete mix containing 30% zircon sand is shown in Fig 10. The XRD pattern at normal temperature showed the CH and CSH as the main hydration products. The increased intensity of the CSH peaks indicate the effect of nano-alumina in increasing the hydration. The improved CSH formation has led to the increase in the mechanical strength and reduction in the porosity of the concrete. The X-ray diffraction pattern at increasing temperature clearly shows reduced CH and CSH crystals with a corresponding increase in the silica and quartz

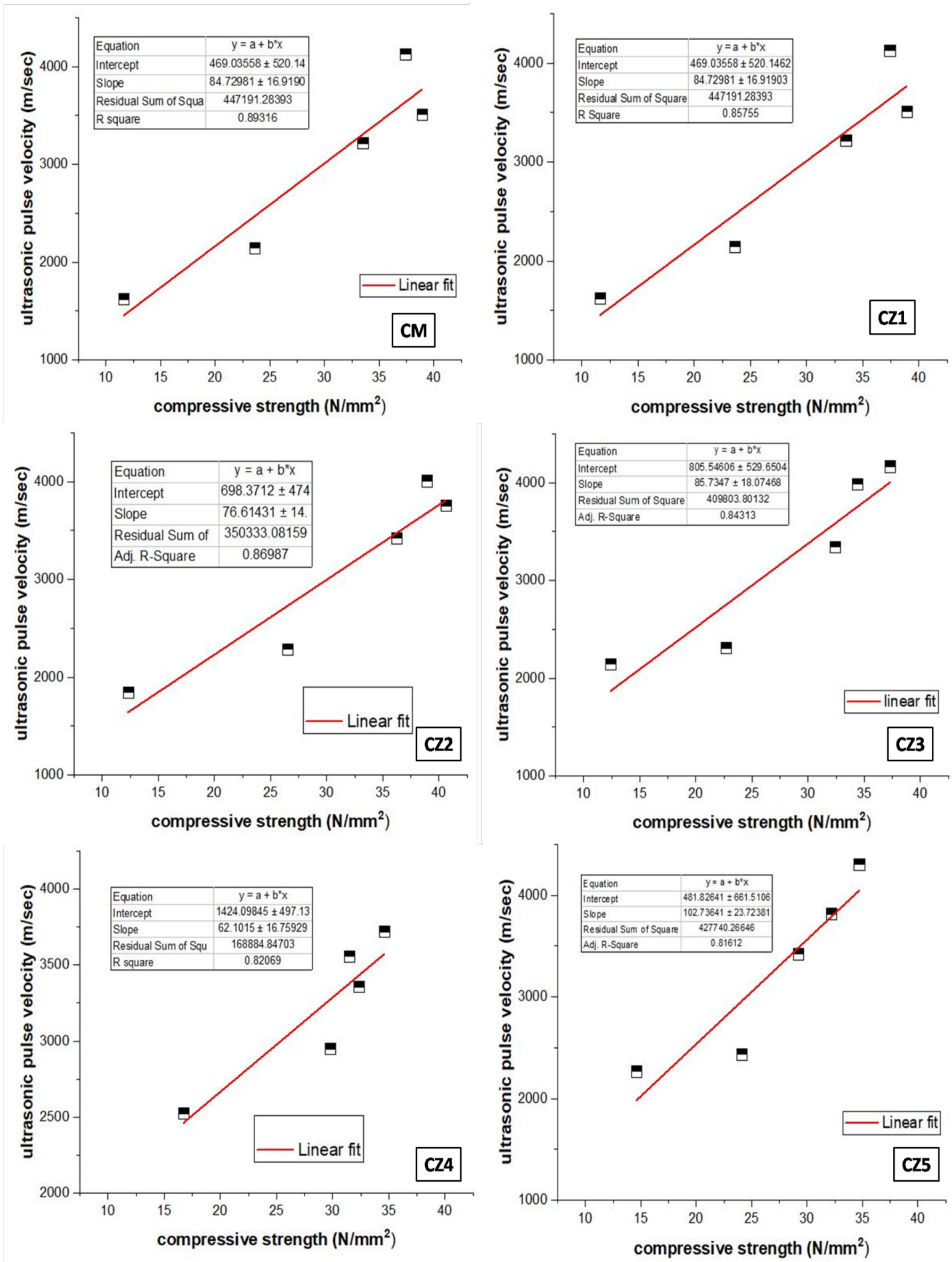

Fig 9 - Relation between compressive strength and ultrasonic pulse velocity of various concrete mixes.

peak. After 400^{0}C almost all the peaks corresponding to CH crystals clearly vanished and only the peaks corresponding to the quartz appears. The XRD results thus shows that the reduction in the strength of the concrete is due to the loss in the crystal structure of all the hydrated phases, CH and CSH crystals.

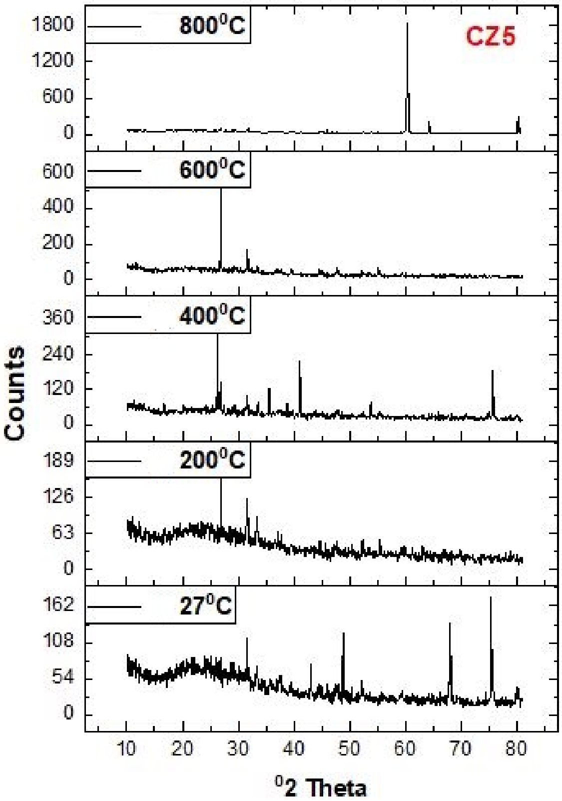

Fig. 10- XRD patterns of the concrete mixes at different temperature.

4.8 SEM

The scanning electron microscope images of the concrete containing 30% zircon sand at normal and after heating to 800^{0}C is shown in Fig 11. The presence of CH crystals can be identified through the white balls of hydrated component present in the SEM images. The formation of CH is the result of the reaction between the pozzolans. The laminar morphology of the CSH gels was also clearly evident from the SEM images. The presence of well developed hydration products was also evident through the EDX spectra as shown in Fig 12. It can be seen that the incorporation of nano-alumina transformed the CH crystals into CSH gels that surrounded the fine aggregates thus forming denser and more compact microstructure. The higher surface energy of the nano-alumina also improved the contact between the cement paste and the aggregates by reducing the distance between the aggregates and the cement particles. The SEM images also shows the interlocking effect exhibited by the nano-alumina and the zircon sand

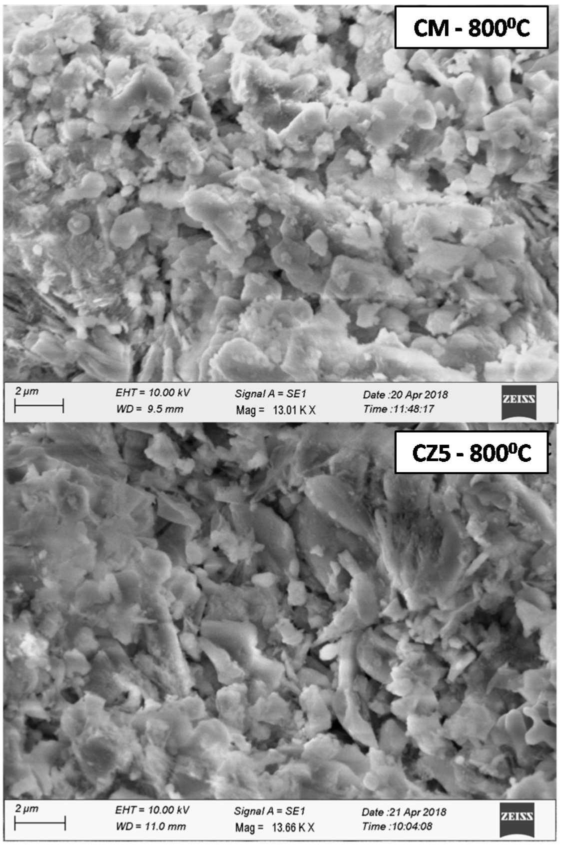

Fig. 11 - SEM images of the concrete mixes.

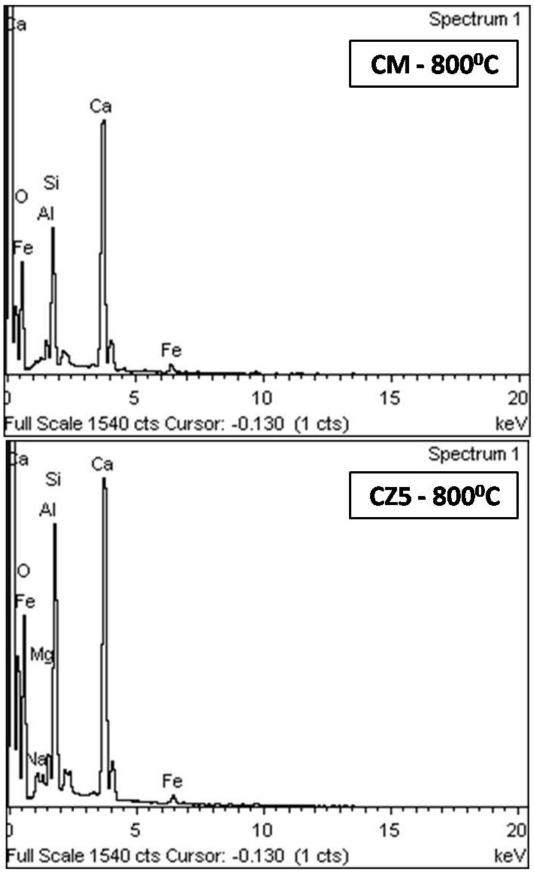

Fig. 12 - EDAX spectra of various concrete mixes.

which stands as evidence to the above stated results. The presence of deformed CSH gels were clearly evident in the SEM images at 800^{0}C which showed the greater formation of CSH gels due to the loss in the crystalline structure of the $Ca(OH)_2$ and CSH crystals. The increased porosity of the thermally treated concrete mixes also shows the disrupted CSH gels and deformed CH crystals which led to the decrement in the strength values. Thus the SEM microstructure results were consistent to the mechanical and porosity results obtained.

5. Conclusion

The following are the conclusions that can be drawn from the experimental results:

1. The slump of the concrete was found to decrease in the nano-alumina substituted concrete mixes due to the higher specific surface area of the nano particles whereas the zircon sand favours the increase in workability.
2. The increase in the compressive strength and flexural strength can be obtained by using nano-alumina in combination with zircon sand. The strength decrement was also gradual in the concrete mixes containing zircon sand and nano-alumina. The sufficient CSH gel formation is a causative agent of this strength increase.
3. The ultrasonic pulse velocity of concrete mixes decreased and the porosity increased with increasing temperature due to the release of water molecules from the concrete structure. The decrease is more severe at 800^{0}C due to the disrupting CH in the matrix. However the increasing zircon sand minimized the effect to a certain extent.
4. The deformation of $Ca(OH)_2$ and disruption of CSH gels can be seen in the SEM images of the concrete at 800^{0}C. The XRD peaks at increasing temperature also reduced the intensity of CH and CSH peaks with increasing temperature.

This study thus clearly demonstrated the effects of increasing temperature on the properties of nano-alumina concrete with fine aggregate substituted by zircon sand. Thus it can be finally concluded that concretes containing nano-alumina and zircon sand can be used to withstand high temperature application.

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