International Journal of Research Publication and Reviews

Journal homepage: www.ijrpr.com ISSN 2582-7421

Impact of Nano Titanium Dioxide on Geopolymer Concrete

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ABSTRACT

Production of Portland cement is increasing every year with the increasing demand of construction. This Portland cement production accounts for about 6 to 7% of all co2 emissions, because approximately one tone of co2 is emitted by the production of one tone of Portland cement. This high concentration of co2 in the atmosphere along with other green house gases causing the global warming. In terms of reducing this global warming, the geopolymer technology could reduce the co2 emission into the atmosphere cause by cement and aggregates industries by about 80- 90 %.Geopolymer concrete is extremely durable and environmentally friendly it decreases the carbon foot print by 90% it is manufactured using industrial waste like GGBS and fly ash along with some alkaline liquids. By using geopolymer concrete we can reduce the usage of cement which results in minimizes the emission of green house gases into the atmosphere.

In this research study, the impact of addition of 0-5% Nano Titanium dioxide on strength properties of geopolymer concrete using individually only fly ash and GGBS are investigated. Compressive strength was determined 7, 28,56,90 days. Along with compressive strength, split tensile strength, flexural strength and durability of geopolymer concrete was observed against sulphate attack and chloride attack. The Highest day 28 days compressive strength was observed in mix FA-NT-5 and mix GGBS-FN-3. The effect of nano titanium dioxide addition on the strength development is shown at 5% of Tio2 in fly ash based geopolymer concrete and at 3% of Tio2 in GGBS based geopolymer concrete.There was also less reduction in mass and compressive strength after emersion in sulphate and chloride solutions so there is very less sulphate and chloride attack on geopolymer concrete specimens

Keywords: Fly Ash, GGBS, Geopolymer, Tio2, Polymers, Green House gases

I.INTRODUCTION

The climate change due to global warming, one of the greatest environmental issues has become a major concern during the last decade. The global warming is caused by the emission of greenhouse gases, such as CO_2, to the atmosphere by human activities. The global release of CO_2 from all sources estimated at 23 billion tonnes a year and the Portland cement production accounts for about 6 to 7% of all CO_2 emissions, because the production of one ton of Portland cement emits approximately one ton of CO_2 into the atmosphere.

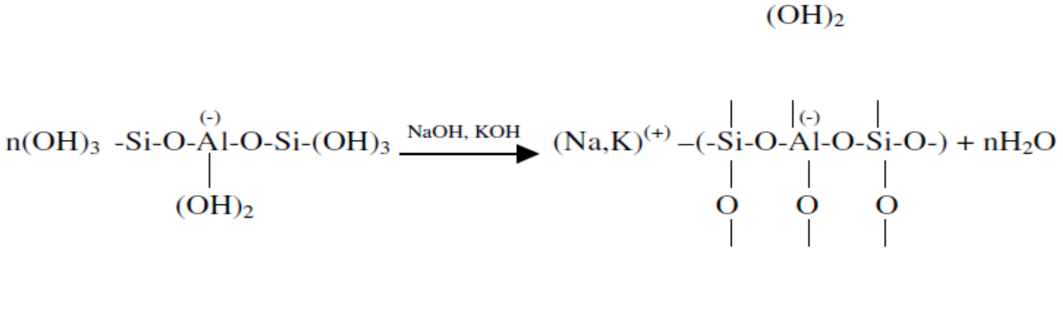
Although the use of Portland cement is still unavoidable until the foreseeable future, many efforts are being made in order to reduce the use of Portland cement in concrete. These efforts include the utilisation of supplementary cementing materials such as fly ash, silica fume, granulated blast furnace slag, rice-husk ash and metakaolin, and finding alternative binders to Portland cement.

In this project work, the geopolymer technology proposed by Davidovits shows considerable promise for application in concrete industry as an alternative binder to the Portland cement.

1.1.TERMINOLOGY AND CHEMISTRY

Geopolymerization involves the chemical reaction of alumino-silicate oxides (Si_2O_5, Al_2O_2) with alkali polysilicates yielding polymeric Si – O – Al bonds. Polysilicates are generally sodium or potassium silicate supplied by chemical industry or manufactured fine silica powder as a by-product of ferro-silicon metallurgy. Equation (1-2) shows an example of polycondensation by alkali into poly (sialate-siloxo).

The last term of Equation (1-2) indicates that water is released during the chemical reaction that occurs in the formation of geopolymers. This water is expelled from the mixture during the curing process.



(1-2)

1.2. SOURCE MATERIALS AND ALKALINE LIQUIDS

There are two main constituents of geopolymers, namely the source materials and the alkaline liquids. The source materials for geopolymers based on alumino-silicate should be rich in silicon (Si) and aluminium (Al). These could be natural minerals such as kaolinite, clays, micas, and alousite, spinel, etc whose empirical formula contains Si, Al, and oxygen (O). Alternatively industrial by-product materials such as fly ash, silica fume, slag, rice-husk ash, red mud, etc could be used as source materials. The choice of the source materials for making geopolymers depends on factors such as availability, cost, and type of application and specific demand of the end users. The alkaline liquids are from soluble alkali metals that are usually Sodium or Potassium based. Sodium based alkaline liquids are cheaper than potassium based alkaline liquids.

1.3 NANO MATERIALS

Nano scale materials are defined as a set of substances where at least one dimension is less than approximately 100 Nano meters. A Nano meter is one millionth of a millimetre – approximately 100,000 times smaller than the diameter of a human hair. Nano materials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields. Recently Nano Technology has been introduced in Civil Engineering applications. Nano technology is one of the most promising areas of science. The use of Nano materials in concrete is new revolution owing to their fine particle size, high reactivity, and specific functional properties. Researchers are taking the chance to gain advantage on Nanotechnology to innovate a new generation of concrete materials that overcome the above drawbacks and trying to achieve the sustainable concrete structures. Evolution of materials is need of the day for improved or better performance for special engineering applications and modifying the bulk state of materials in terms of composition or microstructure or Nanostructure has been the established route for synthesizing new materials.

1.4 EFFECTS OF NANO TITANIUM DIOXIDE ON FRESH AND HARDENED PROPERTIES OF CONCRETE

Titanium oxide (TiO_2) is also known as titania, is the naturally occurring oxide of titanium. The chemical formula for titania is TiO_2. When used as a pigment, it is called titanium white. It has a wide range of applications, from paint to sunscreen to food colouring. Titanium dioxide occurs in nature as well-known minerals rutile, anatase and brookite. It is mainly sourced from ilmenite ore. This is the most widespread form of titanium dioxide-bearing ore around the world. Rutile is the next most abundant and contains around 98% titanium dioxide in the ore.

1.5 SEGREGATION AND BLEEDING

Nano titanium dioxide reduces bleeding significantly because free water is consumed in wetting of large surface area of Nano titanium dioxide and hence the free water left in the mix for bleeding also decreases. Nano titanium dioxide also blocks the pores in the fresh concrete, so water within the concrete is not allowed to come to the surface.

The incorporation of TiO_2 in geopolymer concrete promotes the formation of geopolymer and results in compact microstructure by decreasing the quantity of inner micro cracks. Nano TiO_2 enhances both the early and later compressive strength of geopolymer concrete. Nano-TiO_2 accelerates the formation of geopolymer and refines the microstructure. Nano-TiO_2 improves the carbonation resistance of geopolymer. Nano-TiO_2 reduces the drying shrinkage of geopolymer. The addition of Nano-TiO_2 into the AASP enhances the compressive and the flexural strength of the paste, and improves the flexural to compressive strength ratio as well. Nano TiO_2 improves the mechanical strength and shrinkage property of alkali activated slag paste (AASP).

II.EXPERIMENTAL PROGRAMME

The main aim of this study is to investigate the influence of the addition of Nano-titanium dioxide on the strength and durability properties of Fly ash and GGBS based geopolymer concrete individually.

The various tests performed on concrete samples, followed by a brief description about mix design and curing procedure adopted are given below. Following strength properties of concrete such as compressive strength, split tensile strength and flexural strength of concrete and durability properties such as sulphate attack & chloride attack have been discussed.

2.1.MATERIALS

The materials used for making geopolymer concrete specimens are low-calcium fly ash, GGBS as the source materials, aggregates, alkaline liquids, Nano titanium dioxide.

2.2. Fly Ash

Fly ash is a by-product of the combustion of pulverized coal in thermal power plants. In this work class F Fly ash is obtained from Rajarajeshwari ready mix plant at Kurnool, Andhra Pradesh, India.

2.3. GGBS

Ground granulated blast furnace slag (GGBS) is a by-product from the blast-furnaces used to make iron. GGBS consists essential silicates and alumino silicates of calcium. GGBS obtained from JSW steel Ltd, Gadivemula

2.4. AGGREGATE

Aggregates are the important ingredient materials in concrete. They occupy 70 to 80 percent of the total volume of concrete.

2.5. FINE AGGREGATES

Locally available sand from the River Tungabhadra bed was used. The following tests are conducted on fine aggregate according to IS: 383-1987 [18].Tests on fine Aggregate a**)**Sieve Analysis of Fine Aggregate **b)** Specific Gravity of Fine Aggregate

2.6. COARSE AGGREGATE

The crushed aggregate was used from the local quarry. In this experiment the aggregate was used of 20mm down and tested as per IS: 2386-1963(I, II, III) specification. The following tests are conducted on coarse aggregate.

Tests on Coarse Aggregate

- Sieve Analysis of Coarse Aggregate
- Specific Gravity of Coarse Aggregate

2.7. Alkaline Solution

2.7.1 Sodium Hydroxide

Generally, the sodium hydroxide is available in solid state by means of pellets and flakes form as shown in the Figure 1. The cost of the sodium hydroxide is varied according to the purity of the sodium hydroxide. Since geopolymer concrete is heterogeneous material and its main process is to activate the sodium silicate, sodium hydroxide is used in pellets form. NaOH is recommended to use is of 97-98 percent pureness. The solution of NaOH was formed by dissolving it in water with different molarity. It is recommended that NaOH solution should be made 24 hours before casting and should be used with 36 hours of mixing the pellets with water as after that it is converted to semi-solid state.

Fig. 1 Sodium Hydroxide pellets

2.7.2 Sodium Silicate

Sodium Silicate is available in gel form as shown in Figure 2. In present investigation, sodium silicate 2 (ratio between Na_2O to SiO_2) is used. As per the manufacturer, silicate was supplied to the detergent industry company and textile industry as bonding agent, same sodium silicate is used for making for geo polymer concrete.

2.7.3 Nano Titanium dioxide

In this experimental study Nano titanium dioxide asshown in Figure 6is used. Nano materials are high reactive materials in concrete and they densify the microstructure and reduce the porosity. Chemical composition of Nano TiO_2 contains of 59.93% titanium and 40.55% oxygen.

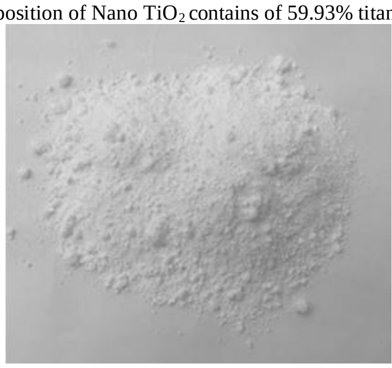


Fig. 2 Nano TiO_2

2.8. **PREPARATION OF ALKALI ACTIVATOR**

The preparation of alkaline activator solution plays a major role in Geopolymer concrete. The AAS is the combination of sodium hydroxide (NaOH) solution and sodium silicate (Na_2SiO_3) solution. The sodium hydroxide (NaOH) solids were dissolved in water to make the solution. The mass of NaOH solids in a solution varied depending on the concentration of the solution expressed in terms of molar, “M”. In this study, NaOH solution with a concentration of 10M consisted of 10x40 = 400 grams of NaOH solids (in flake or pellet form) per litre of the solution, where 40 is the molecular weight of NaOH. The mass of NaOH solids was measured as 285 grams per kg of NaOH solution of 10M concentration. Note that the mass of NaOH solids was only a fraction of the mass of the NaOH solution and water was the major component.

2.9 MIX DESIGN OF GEOPOLYMER CONCRETE

The mix design of geopolmer concrete is entirely different to that of OPC concrete. The production of Geopolmer concrete was carried out by using the trial-and-error method. In GPC, generally the mass of combined aggregates may be taken to be between 70% to 80%. With regard to alkaline liquid to fly ash ratio by mass of fly ash, values in range of 0.35 to 0.6 are recommended. In the first phase of study, the alkaline solutions ratio i.e. sodium silicate to sodium hydroxide are varied in the ratio of 1.5 to 3.5 by mass with increment of 0.5. Table 1 represents the mix proportions of different alkaline activator ratios of geopolymer concrete of M10 molarity. Table 2 represents the details of compressive strength vs. alkaline activator ratio in FAGPC and GGBS based GPC. It was noticed that GPC with alkaline activator ratio 2.5 attains maximum compressive strength. Hence keep constant alkaline ratio 2.5 for further study. Fig 3 represents the variation of compressive strength of FAGPC and GGBS GPC at different alkaline activator ratios.

Table 1 Mix proportions of different alkaline activator ratios in GPC with 10M

Mix No	Na_2SiO_3 / NaOH	Binder (Kg/ m^3)	Mass of F.A (Kg/m^3)	Mass of C.A (Kg/m^3)	Mass of Na_2SiO_3 (Kg/m^3)	Mass of NaOH pellets (Kg/m^3)	Mass of water in NaOH Solution (Kg/m^3)
1	1.5	356.12	554.4	1293.6	117.52	22.38	55.96
2	2	356.12	554.4	1293.6	130.58	18.65	46.63
3	**2.5**	**356.12**	**554.4**	**1293.6**	**139.90**	**15.98**	**39.97**
4	3	356.12	554.4	1293.6	146.90	13.98	34.97
5	3.5	356.12	554.4	1293.6	152.34	12.43	31.09

Table 2 Compressive strengths of FAGPC and GGBS GPC for different alkaline activator ratios

Mix no	Na_2SiO_3/NaOH	Compressive Strength in Fly ash based GPC	Compressive Strength in GGBS based GPC
1	1.5	23.44	50.4
2	2	27.7	55.3
3	**2.5**	**29.92**	**61.11**
4	3	29.32	60
5	3.5	28.73	55.74

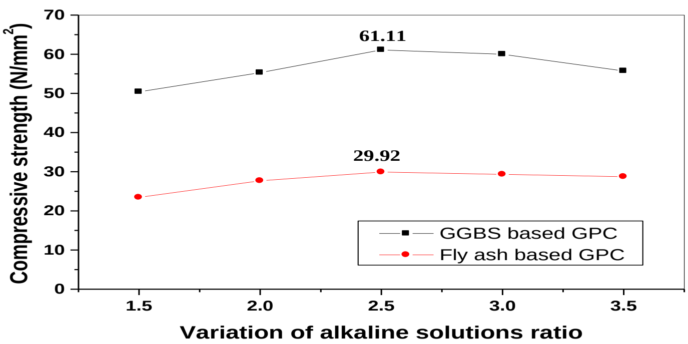


Fig. 3 variation of compressive strengths of FAGPC and GGBS GPC for different alkaline activator ratios

2.9.1TEST PROGRAMME

Inthe present study, the effects of the addition of 0-5% nano titanium dioxide on the strength and durabilityproperties of geopolymer concrete using individually only fly ash and GGBS are investigated. Strength properties of geopolymer concrete such as compressive strength, Flexural strength and split tensile strength are observed. Durability properties of geopolymer concrete such as Sulphate and Chloride attack tests are discussed. The details of different mixes cast were given in Table 3

Mix No.	Mix designation	Flyash Kg/m^3	GGBS Kg/m^3	F.A Kg/m^3	C.A Kg/m^3	Liquid/ Binder	Nano TiO_2 added	NaOH Kg/m^3	Na_2SiO_3 Kg/m^3	Curing
1	FA-NT-0 (Reference GPC mix)	356.12	-	554.4	1293.6	0.55	0	55.96	139.90	60^0c,48 h
2	FA-NT-1	356.12	-	554.4	1293.6	0.55	1	55.96	139.90	60^0c,48 h
3	FA-NT-2	356.12	-	554.4	1293.6	0.55	2	55.96	139.90	60^0c,48 h
4	FA-NT-3	356.12	-	554.4	1293.6	0.55	3	55.96	139.90	60^0c,48 h
5	FA-NT-4	356.12	-	554.4	1293.6	0.55	4	55.96	139.90	60^0c,48 h
6	FA-NT-5	356.12	-	554.4	1293.6	0.55	5	55.96	139.90	60^0c,48 h
7	GGBS-NT-0 (Reference GPC mix)	-	356.12	554.4	1293.6	0.55	0	55.96	139.90	-
8	GGBS-NT-1	-	356.12	554.4	1293.6	0.55	1	55.96	139.90	-
9	GGBS-NT-2	-	356.12	554.4	1293.6	0.55	2	55.96	139.90	-
10	GGBS-NT-3	-	356.12	554.4	1293.6	0.55	3	55.96	139.90	-
11	GGBS-NT-4	-	356.12	554.4	1293.6	0.55	4	55.96	139.90	-
12	GGBS-NT-5	-	356.12	554.4	1293.6	0.55	5	55.96	139.90	-

Table 3.mix proportions of different mixes

2.10. PREPARATION OF FRESH CONCRETE AND CASTING

The dry materials such as fly ash, GGBS and the aggregates were first mixed together in the pan mixer for about 3 minutes. Alkaline activator is prepared using NaOH of 10 molar concentrations mixed with Na_2SiO_3 solution in the ratio of 1:2.5 (by weight) to make the alkali activator fluid. Nano titanium dioxide with 1%, 2%, 3%, 4% and 5% of binder by weight was also added to the fluid. The liquid component of the mixture was then added to the dry materials and the mixing continued for further about 3 minutes to manufacture the fresh concrete.

Geopolymer Concrete specimens are cast on fresh which include cubes for compression test, cylinders for split tensile test and beam for flexural test. During casting the mould should be clean and properly oiled then fresh concrete is placed in the moulds in 3 layers and each layer is tamped and vibrated on vibration table**.** Demoulding is done after the setting of geopolymer concrete. Fig 4 represents the mixing, casting, curing of geopolymer concrete specimens.

Fig. 4 Mixing, Casting, Curing of Geopolymer concrete

2.11. Curing methodology

The GGBS based geopolymer concrete specimens are removed from the mould after 24 h of casting and are cured at ambient temperature (27 ± 2 ℃) until the testing. However, the specimens of all fly ash based geopolymer concrete samples are cured at a 60 ℃ temperature for 48 h within the hot air oven. Further, these samples are kept at ambient temperature until the test. For GGBS based geopolymer concrete samples oven curing is not necessary, only air curing is done.

- **MIX DESIGNATIONS**

FA-NT-0 - Fly ash without Nano titanium dioxide
FA-NT-1 - Fly ash + 1% of Nano titanium dioxide
FA-NT-2 - Fly ash + 2% of Nano titanium dioxide
FA-NT-3 - Fly ash + 3% of Nano titanium dioxide
FA-NT-4 - Fly ash + 4% of Nano titanium dioxide
FA-NT-5 - Fly ash + 5% of Nano titanium dioxide
GGBS-NT-0 - GGBS without Nano titanium dioxide
GGBS-NT-1 - GGBS +1% of Nano titanium dioxide
GGBS-NT-2 - GGBS + 2% of Nano titanium dioxide
GGBS-NT-3 - GGBS + 3% of Nano titanium dioxide
GGBS-NT-4 - GGBS + 4% of Nano titanium dioxide
GGBS-NT-5 - GGBS + 5% of Nano titanium dioxide

III. RESULTS AND CONCLUSIONS

3.1. COMPRESSIVE STRENGTH

The compressive strength of fly ash based geopolymer concrete mixes with different percentage variation of Nano titanium dioxide from 0 to 5% are shown below.

Mix designation	Compressive strength(N/mm^2)	
	7 days	28 days
FA-NT 0 (Reference FA GPC mix)	28.85	34.78
FA-NT 1	38.40	41.02
FA-NT 2	39.57	43.75
FA-NT 3	44.37	47.28
FA-NT 4	45.28	49.84
FA-NT 5	47.77	53.67

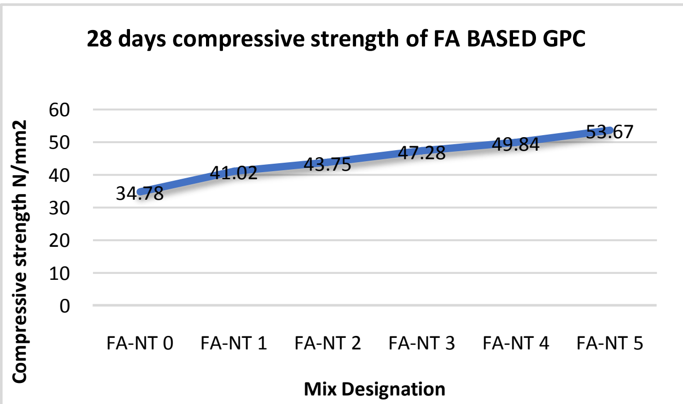


Fig.5 Variation of Compressive Strength of Fly ash Geopolymer Concrete with Nano TiO_2

The compressive strength of GGBS based geopolymer concrete at the age of 7 and 28 days is shown below.

Mix designation	Compressive Strength(N/mm^2)	
	7 days	28 days
GGBS-NT 0 (Reference GGBS GPC mix)	58.05	67.34
GGBS-NT 1	63.71	76.32
GGBS-NT 2	64.78	78.95
GGBS-NT 3	66.88	82.73
GGBS-NT 4	63.45	74.35
GGBS-NT 5	59.21	68.07

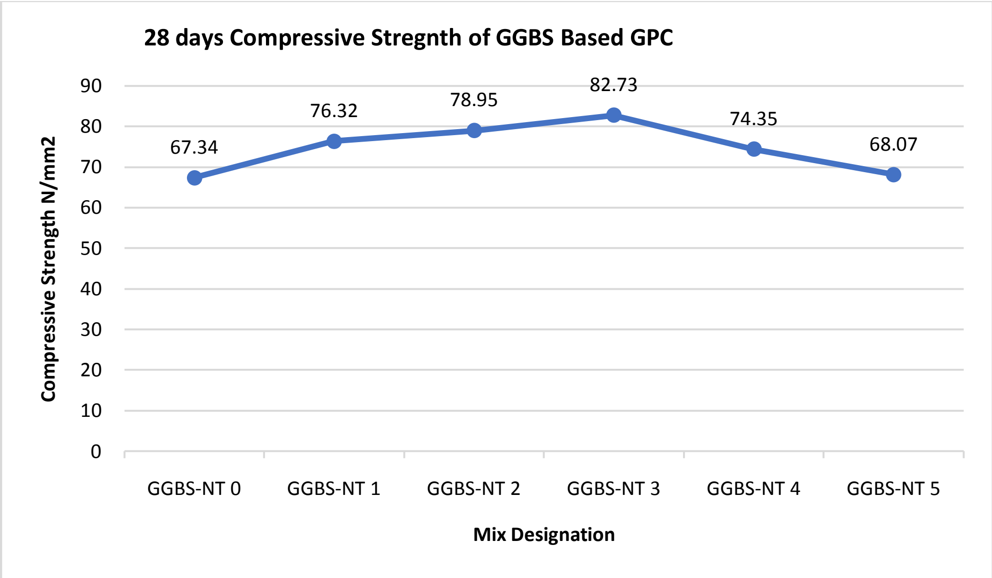


Fig.6. Variation of Compressive Strength of GGBS Geopolymer Concrete with Nano titanium dioxide

3.2. SPLIT TENSILE STRENGTH OF CONCRETE

The Split tensile strength of only fly ash geopolymer concrete & GGBS based geopolymer concrete with 0-5% Nano titanium dioxide at the age of 28 days are shown in Table.

Mix designation	Split Tensile Strength (MPa)
	28 days
FA-NT 0 (Reference FA GPC mix)	2.86
FA-NT 1	3.08
FA-NT 2	3.145
FA-NT 3	3.18
FA-NT 4	3.34
FA-NT 5	3.49
GGBS-NT 0 (Reference GGBS GPC mix)	4.03
GGBS-NT 1	4.34
GGBS-NT 2	4.45
GGBS-NT 3	4.62
GGBS-NT 4	4.27
GGBS-NT 5	4.13

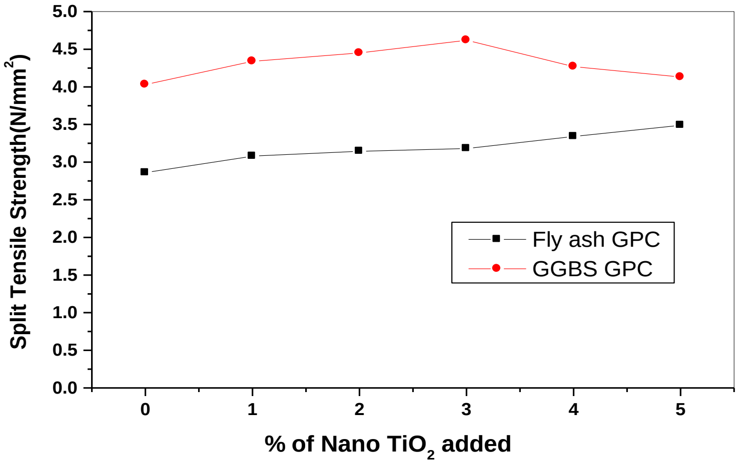


Fig.7Variation of Compressive Strength of GGBS Geopolymer Concrete with Nano titanium dioxide

3.3.FLEXURAL STRENGTH OF CONCRETE

The flexural strengths of only fly ash geopolmer concrete & GGBS based geopolymer concrete with the addition of 0-5% Nano titanium dioxide at the age of 28 days is presented in Table.

Mix designation	**Split Tensile Strength(MPa)**
	28 days
FA-NT 0 (Reference FA GPC mix)	2.86
FA-NT 1	3.08
FA-NT 2	3.145
FA-NT 3	3.18
FA-NT 4	3.34
FA-NT 5	3.49
GGBS-NT 0 (Reference GGBS GPC mix)	4.03
GGBS-NT 1	4.34
GGBS-NT 2	4.45
GGBS-NT 3	4.62
GGBS-NT 4	4.27
GGBS-NT 5	4.13

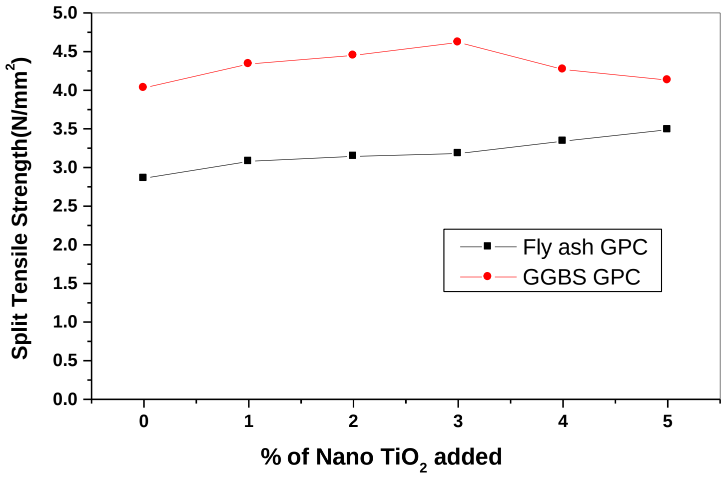


Fig. 8 variation of 28 days Split tensile strength of various Geopolymer Concrete mixes

3.4. SULPHATE ATTACK ON GEOPOLYMER CONCRETE

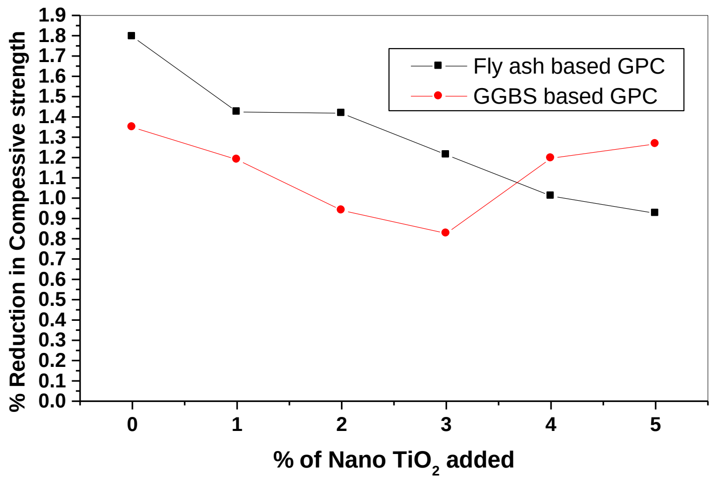


Fig. 9 variation of compressive strength of FAGPC and GGBS based GPC with and without immersion in solution magnesium sulphate

3.5.CHLORIDE ATTACK ON FAGPC

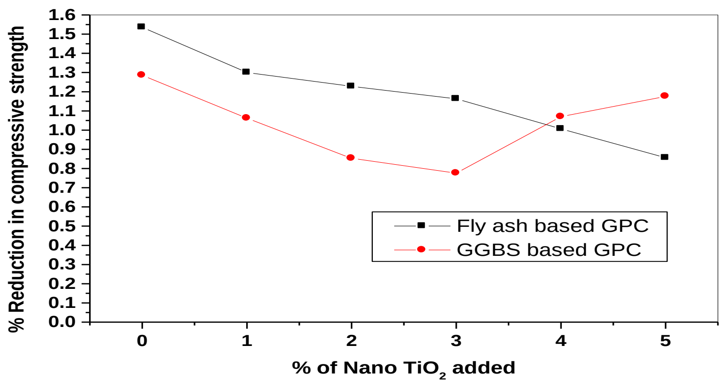


Fig 10 % reduction in compressive strength of GPC after immersion in NaCl solution

CONCLUSIONS

Based on experimental results the following conlusions are drawn

- In this study fly ash and GGBS individually used as base materials for geopolymer concrete and activated with the combination of sodium hydroxide and sodium silicate solutions.
- As a preliminary study GPC (both FAGPC& GGBSGPC), with 10M was carried out for dissimilar ratios of sodium silicate and sodium hydroxide solutions between 1.5 to 3.5.
- Out of all mixes the alkaline activator ratio at 2.5 maximum compressive strength was obtained for both FAGPC and GGBS GPC. This ratio was kept constant for further study
- In the main study the influence of Nano Titanium dioxide on the strength and durability properties in different types of geopolymer concrete has been investigated.
- Nano Titanium dioxide was added 0-5% rates in the fly ash based geopolymer concrete and GGBS based geopolymer concrete individually.
- The strength properties such as Compressive, Split Tensile and Flexural Strengths and durability studies such as sulphate attack and chloride attack were studied up to the age of 28 days. Strength properties of only fly ash-based GPC with Nano Titanium dioxide have a considerable improvement over the control GPC mix.
- Based on the limited experimental study, it was concluded that, at 5% Nano TiO_2 in FAGPC (48 hours oven curing at 60^0c) compressive strength improved 54.31% over control GPC mix. Similarly Split Tensile and Flexural Strengths improved 22.22% and 32.63% over respective control GPC mix.
- Strength properties of only GGBS based GPC with Nano Titanium dioxide have a considerable improvement over the control GPC mix.
- It was observed that, at 3% Nano TiO_2 in GGBS based GPC (ambient curing) improved compressive strength, Split tensile strength and flexural strength of 21.5%, 17.5% and 14.76% over Control GPC mix.
- By adding Nano TiO_2 percentage strength improvement was more in fly ash-based GPC over GGBS based GPC.
- The addition of nano TiO_2 promotes the polymerization process in geopolymer concrete and produce densified structure with minimum cracks.
- The chloride resistance of GPC enriched with the addition of nano TiO_2 ,and as a result range of concrete permeability for FAGPC falls under moderate and GGBS based GPC falls under very low.
- Sulphates and chloride tests on FAGPC and in GGBS based GPC, revealed that % loss in weight was negligible which indicates that GPC had good resistance against sulphate & chloride attack.
- Lower differences in compressive strength of GPC & Nano TiO2 FAGPC and GGBS GPC after 28 days immersion in sulphate & chloride solutions revealed that GPC have good resistance against sulphate & chloride attack.
- The addition of Nano TiO2 promotes the polymerization process in geopolymer concrete and produce densified structure with minimum cracks.

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