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PERFORMANCE EVALUATION OF CONCRETE USING ULTRA FINE CALCIUM CARBONATE POWDER

Umesh Saini[1], Sitesh Kumar Singh[2]

[1]*M.Tech. Scholar, Civil Engineering Department,Career Point University, Kota, (India)*

[2]*Assistant Professor, Civil Engineering Department,Career Point University, Kota, (India)*

ABSTRACT

In India, the use of limestone powder in cement or concrete has not been in practice due to various reasons, which includes non availability of fine limestone powder commercially, difference in the cements of India than those of the developed country etc. But, now with the development of technological advances and their fast adoption by Indian manufacturers now commercial products of calcium carbonate powders with various finenesses are being made available in Indian market.. Investigations report that the effect of limestone powder addition in concrete is more beneficial in concretes containing fly ash.In the present study, a commercially available ultrafine calcium carbonate powder with D_{50}= 2.5 micron is taken and effect of its inclusion in concrete with two different fly ash contents and with two water cement ratios, 0.40 and 0.35 has been investigated on compressive strength from an age of 2 days up to 28 day age and flexural strength at a fixed age.

***Keywords* -** Compressive strength, Density, Flexural strength, etc.

I. INTRODUCTION

The commercial products of calcium carbonate powders with various finenesses are being made available in Indian market. All these factors have set a stage to investigate performance evaluation of ultrafine calcium carbonate powder with Indian cements in Concrete. In India, the use of limestone powder in cement or concrete has not been in practice due to various reasons, which includes non availability of fine limestone powder commercially, difference in the cements of India. But, now with the development of technological advances and their fast adoption by Indian manufacturers, Indian cements have improved. The aim of this paper is to find out how exactly minor additions of limestone powder affect the hydration of OPC and blended fly ash Cement. It is well known that surface treatment of filler can be effective for increasing the bond strength between the filler and the matrix, thereby improving the properties of the composite so here in this study effect of ultrafine limestone powder with cement is to be investigated.

The objectives of the study are:-

1. To observe the effect of addition of ultrafine calcium carbonate powder in cement concrete on compressive strength at early ages 48 hrs, 7 days, 28 days.

2. To observe the possible synergetic effect and compressive and flexural strength (on 45 days) after addition of different combination of fly ash and ultrafine calcium carbonate powder in cement concrete.

II. METHODOLOGY

In order to achieve the objectives of the research and for the development of concepts, which are fundamental for the formation of the whole research work, a comprehensive literature review is made to understand the previous efforts which include the review of text books, periodicals and academic journals, seminars and research papers.The method followed to achieve the objectives of the research determines the required data, which intern is a ground to decide on type and method of data collection and their analysis. Different alternative data collection methods such as experiments, observations are examined and used when proved suitable.

The test results are presented in tabular and graphical forms and the analysis and discussions are also made on the research findings both qualitatively and quantitatively.

Fig.1. Ultrafine calcium carbonate powder (GCC-1250)

2.1Ultrafine calcium carbonate powder

Calcium carbonate ($CaCO_3$) powder is common filler in many industries, including in the cement industry where it is used in the production process. Natural $CaCO_3$ can be obtained from calcite and aragonite in mines. This $CaCO_3$ can be found in limestone, spot disland and other types of rock. Waste $CaCO_3$ powder is produced as a byproduct in stone sawing factories with a typical particle size of 0.5 – 1 µm. $CaCO_3$ powder can also be produced from the reaction of carbon dioxide with calcium hydroxide. Generally, fine limestone particles can enhance the overall particle packing of the binder materials resulting in less space for water between the solid grains. Decreasing the average particle size of limestone used as a partial replacement for cement gave better early-age rheological properties. Above a certain proportion natural impurities in limestone can increase the water demand.

2.2 Limestone powder with fly ash in concrete

The precipitated $CaCO_3$ has a high purity (98 – 99%) and can be produced with a specific crystal morphology. Powdered limestone (Huber Crete® calcium carbonate) has been previously examined as a potential partial replacement for cement. Finally ground limestone with a controlled particle size gives acceptable properties for replacement of up to 10% cement. In addition, it gives higher strength, reduced permeability, and improved workability. However, powdered limestoneis not a pozzolana and reduces compressive strength at higher loadings. Recently, a number of researchers have investigated the use of powdered limestone as a partial replacement of fly ash due to shortages that have cropped up around the world. Such studies have shown an interestingaspect in that the benefits of both materials are utilized while minimizing the downsides. A joint study conducted by researchers at the National Institute of Standards and Technology, the National Research Council of Canada and Purdue University focused on adding fine limestone powder to a high fly ash content concrete. The problems with high fly ash concrete include poor green strength, excessive retardation of the hydration reactions, delayed setting times and low strength. The work postulates that extending the mix with fine limestone powder could be a viable solution to these issues, particularly the hydration retardation and setting issues. They drew a conclusion that the particle sizes ofthe limestone powders are a key variable influencing their performance asaccelerators of reaction and setting; while a nano-limestone is highly efficient in this regard, the 4.4 μm limestone is also effective when used as a 10% volumetric replacement for the fly ash. The key observation in this study is the confirmation of the synergistic interaction between limestone powder and fly ash and its persistence over time. Its study indicated that limestone powder is not inert, but can accelerate the hardening process. The ultrafine limestone powder can act as nucleation sites to result in a high probability of dissolved C-S-H encountering and precipitating on solid particles. They concluded "the fluidity of freshconcrete increases and loss of slump decreases with the ratio of ultrafinelimestone powder to fly ash increasing. Also, when the ratio of limestonepowder to fly ash increases from 5:5 to 9:1, the (W/C) decreasesslightly and the slump of the concrete is stable and the compressive strengthof the concrete remains basically unchanged." In summary, due to both environmental and economic reasons, the availability of fly ash suitable for concrete is restricted. This has led to research into the options to extend the fly ash supply in concrete through the use of ultrafine limestone powders. The research has shown the substitution of ultrafine limestone powders for a portion of the fly ash can result in a synergistic effect on properties that will benefit both the concrete producer as well as the user. In this study, the effect of limestone powder (LP) on the properties of cement concrete has been compared with other mineral additives like fly ash (FA) and their combinations effects. Fresh properties, flexural and compressive strengths and water absorption properties of Concrete are determined. However, the results of this study suggest that certain FA and LP combinations can improve the workability of cement concrete, more than FA, and LP alone. LP can have a positive influence on the mechanical performance at early strength development while fly ash improves aggregate-matrix bond resulting from the formation of a less porous transition zone in concrete.

The viscosity of cement-based material can be improved by decreasing the water/cementitious material ratio (w/c) or using a viscosity-enhancing agent. It can also be improved by increasing the cohesiveness of the paste through the addition of filler, such as limestone. However, excessive addition of fine particles can result in a considerable increase in the specific surface area of the powder, which results in an increase of water demand to achieve a given consistency. On the other hand, for a fixed water content, high powder volume increases interparticle friction due to solid–solid contact. This may affect the ability of the mixture to deform under its own weight and pass through Obstacles. The use of limestone powder can enhance many aspects of cement-based systems through physical or chemical effects. Some physical effects are associated with the small size of limestone particles, which can enhance the packing density of powder and reduce the interstitial void, thus decreasing entrapped water in the system. For example, the use of a continuously graded skeleton of powder is reported to reduce the required powder volume to ensure adequate deformability for concrete .Chemical factors include the effect of limestone filler in supplying ions into the phase solution, thus modifying the kinetics of hydration and the morphology of hydration products Partial replacement of cement by an equal volume of limestone powder with a specific surface area ranging between 500 and 1000m^2/kg resulted in an enhancement in fluidity and a reduction of the yield stress of highly flow able concrete (Yahia 1999). Other investigations have shown that partial replacement of cement by an equal volume of limestone powder varying from 5% to 20% resulted in an enhancement of the fluidity of high-performance concrete having a W/C ratio ranging between 0·30 and 0·40.

Table.1. Chemical composition (wt.%) and the physical characteristics of the fly ash and limestone powder (O'Flaherty & Mangat 1999)

Basic Components	Cement	FA	LP
CaO	67.70	26.96	52.35
SiO_2	19.68	42.14	0.45
Al_2O_3	5.75	19.38	0.33
Fe_2O_3	3.00	4.64	0.14
MgO	0.90	1.78	1.05
Na_2O	0.20	-	0.06
K_2O	0.83	1.13	0.02
SO_3	2.78	2.43	-
Cl	0.01	0.001	-
Loss of Ignition	2.84	1.34	42.50
Free CaO	1.55	4.34	-
Insoluble residue	0.70	-	0.20

The effect of partial replacement of cement with LP on the initial setting time and slump are shown in Figs 2.1 and 2.2 respectively. The initial setting time decreased to about 75 minute for the LP compensate with cement at amounts of (15,20)%, then increased to 90 minute at the maximum amount of compensating (25%). Apart from calcareous filler having a quite limited chemical interaction with hydration product, it has been shown that a chemical reaction of calcite $CaCO_3$ with reactivity appears.yet the extent of calcareous filler chemical activity is generally admitted to be very limited [Hawkins et al, 2003]. As filler generally replaces cement there is a dilution effect, the cement paste amount decrease [Lawrenceetal, 2005], these affected on time of initial setting.

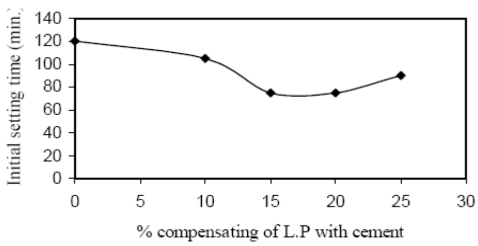
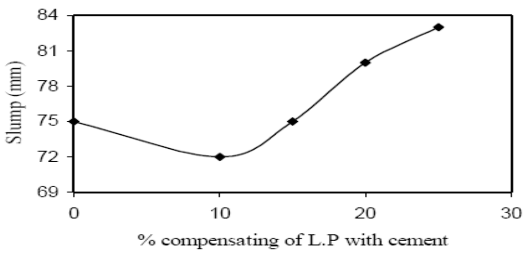


Fig.2. Effect of LP partial replacement with cement on setting time[Benachuretal]

Slump decrease to 72 mm with 10% compensating of cement with LP, and recovered to 75mm at amount 15% of compensating. The increasing of compensating of cement with LP, increase in slump ranged from 7% at 20% of compensating and expanded to 11% at amount 25% of compensating. Water is getting adsorbed at the surface of filler particles. As fillers specific surface is higher than that of sand, slump decrease due to adsorption phenomenon. As filler particles fill up voids, filler occupies the place of sand with smooth surface particles



which reduced the inter particle fraction that increase slump [Benachouretal, 2008].

Fig.3. Effect of LP partial replacement with cement on slump[Benachouretal]

This research study exhibit the feasibility of the use of LP as cement partial replacement in concrete mixes and studies the effect of elevated temperature on the compressive, and flexural strengths. The slump of concrete relatively increases with higher values of the percentage of compensating of cement with LP. Based on the results, it was observed that the compressive strength of concrete increase with the increase in LP compensating, concrete made with 10% LP compensating showed higher compressive strength.

Synergy between fly ash and limestone powder in ternary cements

In this study ternary cements containing ordinary Portland cement (OPC) and different replacement levels of limestone powder and fly ash are investigated. The effect of limestone powder on OPC is twofold. Fine limestone powder exerts a physical filler effect on the OPC hydration. Replacing part of the OPC with limestone will increase the effective water to OPC ratio, and provide additional surface for precipitation of hydration products, thereby promoting the early age hydration of the OPC. Besides the filler effect, there is also a chemical effect, that calcium carbonate of the limestone powder can interact with the aluminate hydrates formed by OPC hydration. The hydration productions from C_3S and C_2S are similar but quantity of calcium hydroxide (lime) released is higher in C_3S compared to C_2S. The reaction of C_3A with water takes place in presence of sulphate ions supplied by dissolution of gypsum present in OPC. By that reaction calciummonosulphoaluminate hydrate (ettringite) is produced.

Formulation of hemicarboaluminate hydrate leads to the stabilization of the ettringite and will result in an increase in the total volume of the hydration products, which potentially might result in a decrease in porosity and thus increase in strength. A clear demonstration of interaction between fly ash and limestonepowder was observed when studying fly ash–limestone–calcium hydroxide mixes prepared with a high alkaline solution (PH = 13.2) then it is seen that more water was bound relative to the fly ash content, and the hydration products formed were altered when lime stone was included in the system. The calcium aluminate hydrates formed during the pozzolanic reaction reacted with the calcium carbonate of the limestone powder, and formed calcium carboaluminatehydrate.

Both for the limestone and fly ash blended cements, the amount of bound water per dry content decreases and the amount of bound water relative to the OPC content increases with increasing replacement level, except for the 3% replacement of the OPC with limestone powder that shows no reduction in the amount of bound water relative to the dry content. The amount of bound water increases as limestone powder and fly ash are combined instead of just using one of them after 28, 90 and 140 days. The maximum amount is obtained for 25% fly ash and 10% limestone powder after 90 and 140 days. The main part of the bound water is bound during the first day and the following 28 days. The amount of bound water increases slightly up to 90 days, but generally does not change thereafter. The calcium hydroxide (CH) content per dry content decreases with increasing limestone or fly ash replacement for the fly ash and limestone blended cements. The calcium hydroxide CH content per OPC increases with increasing limestone or fly ash replacement at 1 day. However at later ages, different trends are observed for limestone and fly ash blended cements. For the limestone blended cements there is a decreasing trend in the CH content per OPC at 5–10% limestone, but the amount tends to increase again at higher replacement levels. For the fly ash blended cement with high fly ash content (>20%) a decrease in CH content can be observed after 28 days. The higher the fly ash content, the more prominent is the CH reduction.

According to the thermogravimetric results two mechanisms can be distinguished: the filler effect related to the increase of the amount of bound water and calcium hydroxide relative to the OPC content with increasing replacement of OPC with limestone. Indeed, replacing OPC with limestone raises the effective water to OPC ratio, and the limestone powder provides additional surface for the precipitation of hydrates; both effects promote hydration and the dilution effect is caused by the reduction in the amount of the most reactive component, OPC, in the system. At replacement levels larger than 5%, the calcium hydroxide per dry content and the compressive strength decreases with increasing replacement of OPC by limestone indicating that the filler effect cannot compensate for the dilution effect at all tested ages.

Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash.

The effect of 3% limestone powder addition on short and long term macroscopical properties is generally small in concrete. Regarding the compressive strength, both enhanced strength and reduced strength have been reported upon limestone addition. A benefit of the addition of small amounts of calcium carbonate powder is a reduction of the expansion observed upon sulphate attack, which is most prominent for cement with high C_3A content. It also leads to a reduction of the optimal gypsum content, which may result in a reduction of raw material costs.

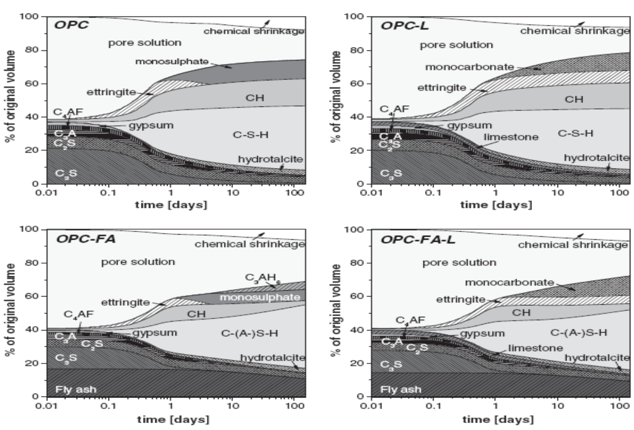


Fig.4. The volume of the different phases as function of time in hydrating cement pastes modelled by GEMS.

III. EXPERIMENTAL PROGRAMME

The main objectives of the experimental program are to study the effects of using ultrafine as cement replacing filler on the performance of concrete. To achieve these objectives, a major experiment was designed. It was performed to determine the effects of replacing part of cement with ultrafine calcium carbonate powder on concrete performance such as workability and strength.

Typical properties	Percentage by wt.
Calcium carbonate content	98%
Magnesium (as MgO) content	0.4%
Iron as Fe_2O_3 content	0.03%
Refractive index	1.57
Particle size, average	0.9 micromtr
PH	8
Density	2.7
Specific surface area	12-15 (m^2/gm)

3.1 Chemical and physical properties of limestone powder

It consists of determination of the mix designing, concrete specimens preparation and tests of fresh and hardened concrete cubes and beams, was designed to determine the effects of replacing part of cement with ultrafine calcium carbonate powder on compressive strength and flexural strength. Here we have done mix design of concrete which containing different proportion of powder like fly ash, GCC-1250, by using the IS code 10262:2009**.** For the experimental purpose OPC 43 grade confirming to IS 8112 was used. In the present study ultrafine limestone powder GCC-1250 is used in concrete. This powder is a grade name of Calcium Carbonate series, manufactured by Indian industry. The unique particle size of this ground calcium carbonate distribution optimizes particle packing leaving less void space to be filled by expensive resin. Used powder is extremely pure and imparts high brightness. Generally, this type of fine limestone powder particles can enhance the overall particle packing of the binder materials resulting in less space for water between the solid grains. For the use of powder in experiment, it's specific gravity is evaluated by Lechatelier's apparatus.

In this study 20 mm and 10 mm aggregate are used. Local Banas sand was used as sand in all concrete mixture in this report. According to sieve analysis sand falling on II zone as per IS: 383-1970.GLENIUM B233 high-performance super plasticizer was used as chemical admixture in all mixtures. GLENIUM B233 is free of chloride & low alkali. It is compatible with all types of cements.

3.2 Mix proportions

Mix proportioning of the concrete mixes has been attempted based on IS 10262-2009 guidelines, further following assumptions have been made to compute the quantities of the cementations materials: Two water cement ratios are selected aiming to produce concretes with 28 day strengths in the range of 40 MPa to 70 MPa possibly. The use of ultrafine powder in concrete is mainly targeted to enhance early age strengths representing moderate to high compressive strength regime.It is planned to investigate the performance under compression and flexure. Effect of addition of the ultrafine powder on early strength and till 45 days age is aimed to be studied. Sample size for compressive strength test and flexural strength test are proposed to be (15x15x15 cm) and (10x10x50cm) respectively. For this 9 cube and 3 beam of each sample are casted.The compressive strengths at ages 48 hours, 7 days, 28 days are planned to be studied. Flexure strength is planned to be studied at 45 days age.

Control mixes:

1.OPC alone for water cement ratio 0.40

2.OPC alone for water cement ratio 0.35

Binary Mixes

OPC+FLYASH COMBINATION:-

1. OPC + flyash (30%) for water cement ratio 0.40
2. OPC + flyash (30%) for water cement ratio 0.35
3. OPC + flyash (40%) for water cement ratio 0.40
4. OPC + flyash (40%) for water cement ratio 0.35

Ternary Mixes

OPC+FLYASH+(30%)+GCC-1250 COMBINATION:-

Table.3. TestResuls Of Strengths Of Samples Obtained For W/C = 0.4

Sample description	Compressive Strength (N/mm^2)			Flexural strength (N/mm^2)
	2 Days	**7 Days**	**28 Days**	**45 Days**
OPC	12.12	25.35	36.85	3.6
OPC + Flyash(30%)	11.50	27.6	41.98	4.20
OPC+Flyash(30%)+ GCC-1250(1%)	13.22	30.47	44.85	4.30
OPC+Flyash(30%)+GCC-1250(2%)	14.37	33.35	49.45	4.50
OPC+Flyash(30%) +GCC-1250(3%)	13.8	31.62	46.57	4.45
OPC + Flyash(40%)	11.5	32.77	48.3	4.20
OPC + Flyash(40%) GCC-1250(1%)	16.10	31.62	46	4.40
OPC + Flyash(40%) GCC-1250(2%)	14.60	32.2	48.87	4.50

OPC + Flyash(40%) GCC-1250(3%)	15.12	33.35	49.94	4.64

Table.4. TestResuls Of Strengths Of Samples Obtained For W/C = 0.35

Sample description	**Compressive Strength (N/mm^2)**			**Flexural strength (N/mm^2)**
	2 Days	**7 Days**	**28 Days**	**45 Days**
OPC	13.35	25.45	38.66	4.00
OPC + Flyash (30%)	14.02	28.65	44.75	4.27
OPC + Flyash (30%) + GCC-1250 (1%)	18.05	32.87	45.76	4.35
OPC + Flyash (30%) + GCC-1250 (2%)	17.75	35.70	46.12	4.55
OPC + Flyash (30%) + GCC-1250 (3%)	19.97	37.45	46.90	4.58
OPC + Flyash (40%)	14.98	31.85	40.60	3.90
OPC + Flyash (40%) + GCC-1250(1%)	15.68	33.35	46.97	4.21
OPC + Flyash (40%) + GCC-1250(2%)	16.45	34.65	48.22	4.61
OPC+ Flyash (40%) + GCC-1250(3%)	15.56	33.35	48.66	4.68

1. OPC+flyash(30%)+GCC-1250(1%)for w/c ratio 0.40
2..OPC+flyash(30%)+GCC-1250(2%) for w/c ratio 0.40
3. OPC+flyash(30%)+GCC-1250 (3%)for w/c ratio 0.40
4. OPC+flyash(30%)+GCC-1250(1%)for w/c ratio 0.35
5. OPC+flyash(30%)+GCC-1250(2%) for w/c ratio 0.35
6. OPC+flyash(30%)+GCC-1250(3%)for w/c ratio 0.35

OPC+FLYASH+(40%)+GCC-1250 COMBINATION:-

S**AME COBINATION FOR ALL W/C RATIO**

COMPRESSIVE STRENGTH AND AGE OF CONCRETE SPECIMEN AND ARE SHOWN:-

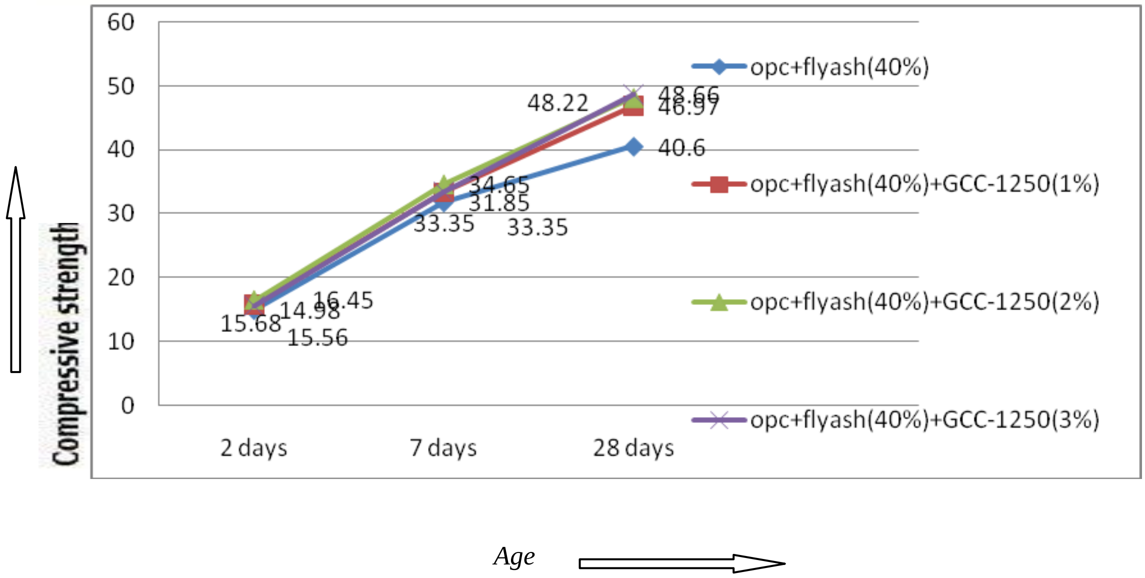


Fig.5. Compressive Strength And Age Of Concrete Specimen

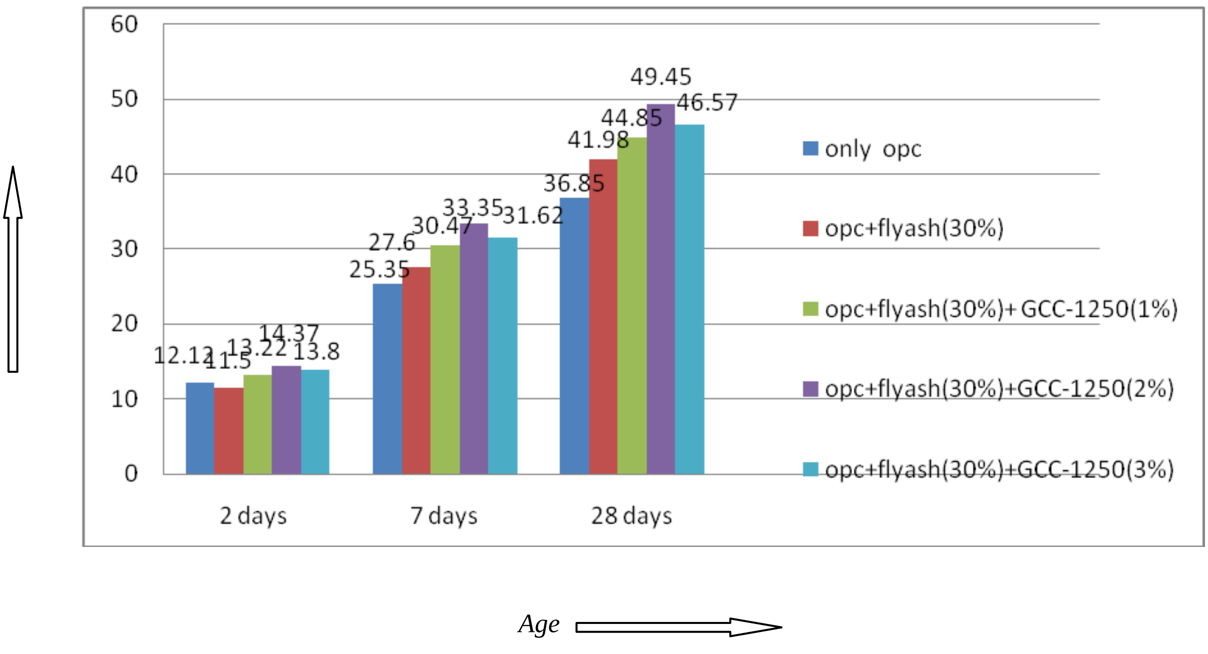


Fig.6. Compressive Strength And Age Of Concrete Specimen

IV. DISCUSSION OF TEST RESULTS

i. It is observed that the compressive strength at early age, i.e. the 2 days age, increases considerably with the addition of the ultrafine powder in the concrete. This increase is of the order of 20-50 % with various w/c and percentages of flyash. This increase in strength at early age is expected to be due to both the reasons- densification of the matrix through micro-filler, and higher degree of hydration in presence of flyash-calcium carbonate system.

ii. Percentage gain in strength within the 7-28 days period are computed and shown in Table 4.3 to Table 4.6. It is observed that the % gain is of the order of 48-50 % in the period, for all the mixes, i.e. with and without the ultrafine powder. It indicates that the gain of strength continues with similar magnitude, even after 7 days age in the ternary systems.

iii. It is observed that slope of line for mix OPC + flyash+ ultrafine powder during the age period 7 days-28 days is more than the concrete which has only OPC powder. It indicates that the rate of gain of compressive strength in the age period 7 days to 28 days is more in the concrete containing flyash- calcium carbonate powder. The literature suggests that the limestone powder particles act as nucleation sites in the cement-flyashsystems , the increase in rate of gain of strength suggests confirmation of the phenomenon in the present study.

iv. With replacing OPC with limestone raises the effective water to OPC ratio, and the limestone powder provides additional surface for the precipitation of hydrates; both effects promote cement particle's hydration.

v. When interpreting these results as the filler effect of the fly ash,It is seen that initially increases the CH/OPC content with increasing fly ash content,However, after 28 days a consumption of CH can be observed for the fly ash blended cements with high fly ash content (>20%).

The variation between compressive and flexural strength and ages for different water cement ratio and different combination of cementitious materials are shown in Fig.7.

Graph between compressive strength and age (w/c=0.40)

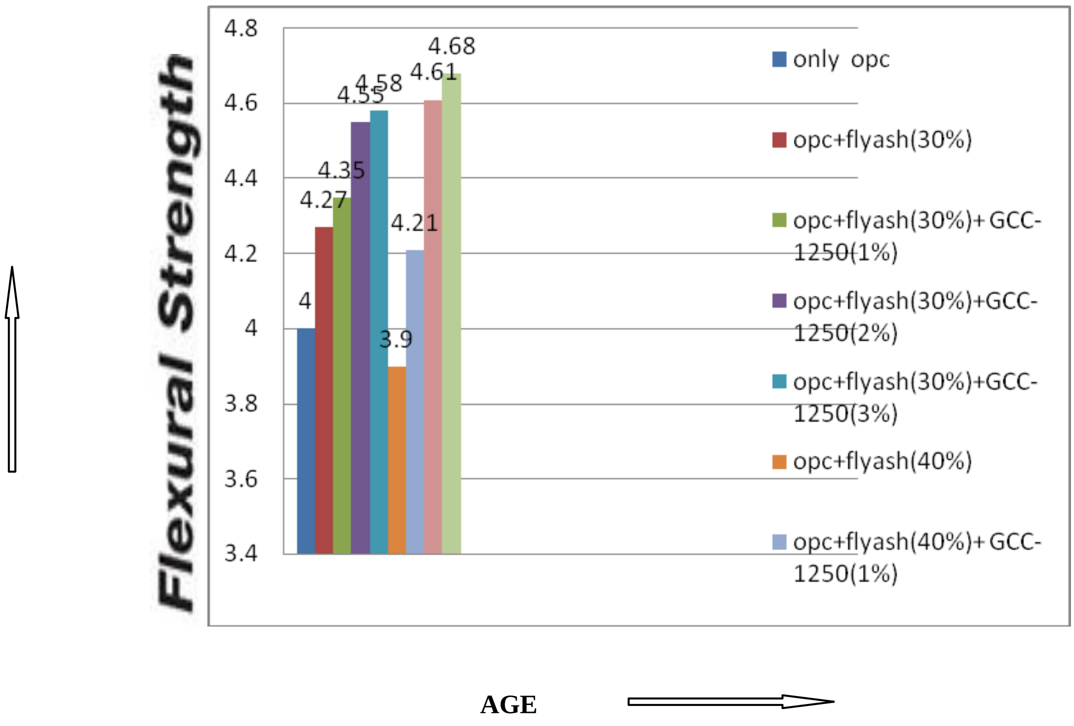


Fig.7. Variation of flexural strength with different set of mixes for w/c=0.40

V. CONCLUSIONS

Based on experimental test results the following conclusions are drawn:

1. In the experiment when flyash is added with cement,compressive and flexural strength both increases .
2. In the experiment when ultrafine powder is used with fly ash, compressive and flexural both increases rapidly as content of ultrafine powder increases in concrete mix.
3. The presence of limestone leads to the formation of mono or hemicarboaluminate hydrates instead of monosulphoaluminate hydrate and stabilizes thereby the ettringite. This leads to an increase in the volume of hydrates and a subsequent decrease in porosity and an increase in strength. Fly ash, on the other hand, can provide additional aluminates which will lower the sulphate/aluminate ratio and thereby amplify the impact of the limestone.
4. The stabilization of ettringite, when limestone is present, leads to an increase in the volume of hydration products, as can be deduced from the chemical shrinkage results, to a decrease in porosity and thus to an increase in compressive strength.
5. By experimental results, it is predicting a significant acceleration of cement hydration only in lower w/c (e.g., 0.35) ratio blended cement pastes. Thus, limestone substitutions are projected to be particularly advantageous in lower w/c (< 0.4) concretes, where the cement clinker being replaced may only be serving the function of a relatively filler material.

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