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Influence of Metakaolin on Chemical Resistance of Low Calcium Fly Ash Based Geopolymer Concrete

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Abstract: The study on cementless concrete is one of the most trending topics in the construction industry. This paper will give an inclusive on the effect of metakaolin on developing a low calcium fly ash (FA) based geopolymer concrete (GPC). Nine mixes were prepared with 30% and 50% replacement of low calcium FA with metakaolin, and molarity (8M, 12M and 16M) of alkaline activator (NaOH). Experiments were conducted on weight loss, residual compressive strength and Ultrasonic pulse velocity (UPV) of the GPC mixes. The experimental results indicated that workability of the mixes reduces with increasing percentage of metakaolin in comparison to the controlled GPC mix (100% low calcium FA). The compressive and tensile strength of geopolymer concrete mix with increasing molarity of NaOH solution and 30 - 50% replacement of fly ash with metakaolin was observed to be enhanced by 10 - 12% and 28 - 34% at 28 and 90 days respectively. The acid resistance values in terms of weight loss, compressive strength and quality of the specimens with 50% metakaolin substitution cured in H2SO4 solution for 56 days with different molarity was higher as compare to the control mixes. Thus, presence of metakaolin in the low calcium based GPC helps in resisting the aggressive chemical ingress in the concrete.

1. Introduction

Cement production is the main reason for CO_2 emission (more than 5%)[1] next to greenhouse gas released globally. Thus, researchers are on quest for replacement of cement in developing sustainable concrete in construction industry. Many of the investigations were on partial substitution of cement by supplementary cementitious materials (SCMs) such as Fly Ash (FA), Ground Granulated Blast Furnace Slag (GGBS), Rice Husk Ash (RHA), Silica Fume (SF), Metakaolin (MK), Copper slag (CS) etc. The chemistry in Ordinary Portland Cement (OPC) the resulting hydrated compounds Calcium Silicate Hydrate (C-S-H) and portlandite ($Ca(OH)_2$) which cause the hardening of the cement matrix are the main reason one could not replace cement in large scale. Class F Fly ash are pozzolanic in nature but due to the low lime content (less than 20%), it needs cementing agent, so it can be replaced up to certain percentage[2,3,4,5]. But 100% cement was replaced with the introduction of geopolymerization technique by J Davidovits[6,7]. The reaction between polymerized alkali-activated and the pozzolanic materials in FA generates hydrated compounds (alkali-crossed linked network) caused due to poly-condensation and hardened the GP concrete. The hydrated compounds in GPC has similar nature compare to conventional cement concrete. Since then, GPC is considered as the third generation cement after lime and cement.

The fly ash-based and metakaolin based GP concrete developed under different curing methods (ambient or oven) in various studies states that GPC are more durable and stronger than concrete made with precursor

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cement due to its resistance to corrosion[8,9,10]. Few papers were reported on synergistic effect fly ash and metakaolin in developing GPC on the mechanical and durability (porosity, pore refinement, resistance to chemical ingress)[11,12,13]. This paper is concentrated on construction of low calcium fly ash –based GPC with partial replacement of FA by MK (0%, 30% and 50%) at different molarity (8M, 12M and 16M) of alkali-activator. And the influence of MK on fresh, hardened, residual compressive strength and weight loss after sulfate attack of GPC.

2. Experimental program

2.1. Materials

2.1.1. Fly Ash

Class F fly ash was used as the base material (ASTM C618). The chemical composition is given in Table 1, with low calcium percentage obtained from local thermal plant in Jalandhar.

2.1.2. Metakaolin

The highly reactive metastable in the form of anhydrous aluminosilicate, metakaolin was used as secondary source of $Al_2Si_2O_7$ (as per ASTM C618). The material was obtained from Astraa Chemicals, Chennai. The chemical composition shown in Table 1.

2.1.3. Alkaline activators

A combination of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) solution waere used as the activator. Both NaOH and Na_2SiO_3 were procured from local dealer (LOBA chemicals) with 98% purity. The concentration of NaOH solution for 8M, 12M and 16M molarity contains 320 g, 361g and 444g of NaOH solids respectively. The physical properties of NaOH and sodium silicate are given in Table 2.

Table 1. Chemical composition of Fly Ash and Metakaolin.

Constituent	Fly ash	Metakaolin
CaO	1.34	0.1
SiO_2	53.36	54.78
Al_2O_3	26.49	40.42
Fe_2O_3	10.86	0.76
SO_3	1.7	0
MgO	0.77	0.41
Na_2O	0.37	-
K_2O	0.8	-
TiO_2	1.47	-
P_2O5	1.43	-
LOI	1.39	-

2.1.4. Aggregates

The details of both the fine and coarse aggregates are given in **Table 3**. Maximum nominal size of coarse aggregate used were 12.5 mm.

Table 2. Properties of NaOH and Na_2SiO_3.

Properties	NaOH	Na_2SiO_3
Molar Mass	40 g/mol	122.06 g/mol
Appearance	White solid	White opaque crystals
Density	2.1 g/cc	2.6 g/cc
Melting point	318 °C	1088 °C
Boiling point	1390 °C	-

Table 3. Properties of coarse and fine aggregate.

Property	Coarse aggregate	Fine aggregate
Specific Gravity	2.78	2.55
Water absorption	0.50%	1%
Fineness modulus	7.21	2.93
Bulk density (kg/m^3)	1.675	1.57
Source	Crush stone	River sand

2.1.5. Super plasticizer
SP-430, a naphthalene sulfonate based super plasticizer was used which was procured from local distributer.

2.2. Methodology
2.2.1. Mixing, casting and curing
The mix was design for G20 (20 MPa) grade i.e., 100% FA based GPC (control mix). The mix proportion for G20 grade GPC is given in Table 4. Three mixes of each 8M, 12M and 16M were with varying percentage of metakaolin i.e., 0%, 30% and 50%. So, a total of nine mixes were prepared as shown in Table 5. The dry materials were mixed thoroughly followed by the activated alkali-solution in to the mixer[14].

Test were performed on the fresh concrete to record the slump value using slump cone penetration method. Then the concrete is cast on a 100 mm cubes for compressive, tensile, UPV and compressive, UPV after acid attack.

To avoid water loss, the samples were wrapped with vinyl sheets during oven curing (60°C) for 24 hours. The specimens were demoulded after 24 hours and allowed to cure under ambient curing for 28 and 90 days.

3. Result and discussion
3.1. Workability
The test conducted on green concrete for different GPC mixes were recorded and represented in Figure 1. It has been observed that workability reduces with percentage increment of metakaolin but with increase in molarity of NaOH solution the slump values increases.

3.2. Mechanical Properties
The compressive strength and tensile strength test were performed on the 100 mm cubes for 28 and 90 days curing age of the GPC mixes. The results were evaluated and projected as in Figure 2 and Figure 3. The replacement of FA by MK has enhanced both the compressive and tensile strength compare to control mix. The maximum strength was obtained at 16F50M50 (16M, FA 50% and MK 50%), improved by 10-12 % at 90 days curing age. Similar pattern was recorded for tensile strength.

Table 4. Quantity of materials for GPC G20 grade.

Parameter	Content
Binder (kg/m^3)	327
Fine aggregate (kg/m^3)	627
Coarse aggregate (kg/m^3)	1248
NaOH (kg/m^3)	54.33
Na_2SiO_3 (kg/m^3)	108.67
Ratio of mixture proportion	1:2.05:3.81
Extra water (kg/m^3)	22
Super plasticizer (kg/m^3)	6
Liquid/ binder ratio	0.5
Slump (mm)	100
Water/GP solids ratio	0.31

Table 5. Mix combination of the GPC mixes (quantity per m^3).

Mix	Fly Ash	Fine aggregate	Coarse aggregate Kg		Metakaolin	NaOH	Na_2SiO_3	Water	SP	L/B
	kg	kg	(20 mm)	(10 mm)	kg	kg	kg	kg	(%)	
8F100M0	327	627	874	374	0	54.3	108.6	22	2	0.5
8F70M30	228.9	627	874	374	98.1	54.3	108.6	22	2	0.5
8F50M50	163.5	627	874	374	163.5	54.3	108.6	22	2	0.5
12F100M0	327	627	874	374	0	54.3	108.6	22	2	0.5
12F70M30	228.9	627	874	374	98.1	54.3	108.6	22	2	0.5
12F50M50	163.5	627	874	374	163.5	54.3	108.6	22	2	0.5
16F100M0	327	627	874	374	0	54.3	108.6	22	2	0.5
16F70M30	228.9	627	874	374	98.1	54.3	108.6	22	2	0.5
16F50M50	163.5	627	874	374	163.5	54.3	108.6	22	2	0.5

Note: SP- superplasticizer, L/B – liquid activator to binder (Fly ash) by mass ratio.

3.3. Acid resistance

After oven curing for 24 hours at 60 °C and ambient curing for 28 days, the samples were then immersed in 1% H_2SO_4 solution for 28 days to determine the loss in mass and loss compressive strength due to deterioration of the GPC specimens. The pH value of the acid was regulated every after 2 days and kept between pH value 2-3. The average of the weighed specimens and compressive strength were measured for valuation. The percentage variation in weight loss and residual compressive strength are shown in Figure 3. It was observed that percentage loss in compressive strength by acid attack is high for mix containing 100%FA (12M) i.e. 8.65% and the percentage loss in compressive strength for mix containing 50%MK + 50%FA (16M) i.e.2.38%. This low % loss in mass and strength can be attributed to the fact that geopolymer concrete do not have free lime content in its matrix geopolymer which are not easily attacked by acid.

However, free lime is not measured in present case, research work indicates that because of nature of reaction occurring in geopolymer concrete, possibility of free lime is very less. Gel formed in reaction of aluminosilicate polymeric system involves no evolution of free lime[15].

3.4. Ultrasonic Pulse Velocity (UPV)

The non-destructive UPV were conducted for both before and after acid attack for 28 days curing (before) and 56 days (after exposure to acid). Figure 4. Represents the comparison of the pulse velocity (quality of the GPC mixes.

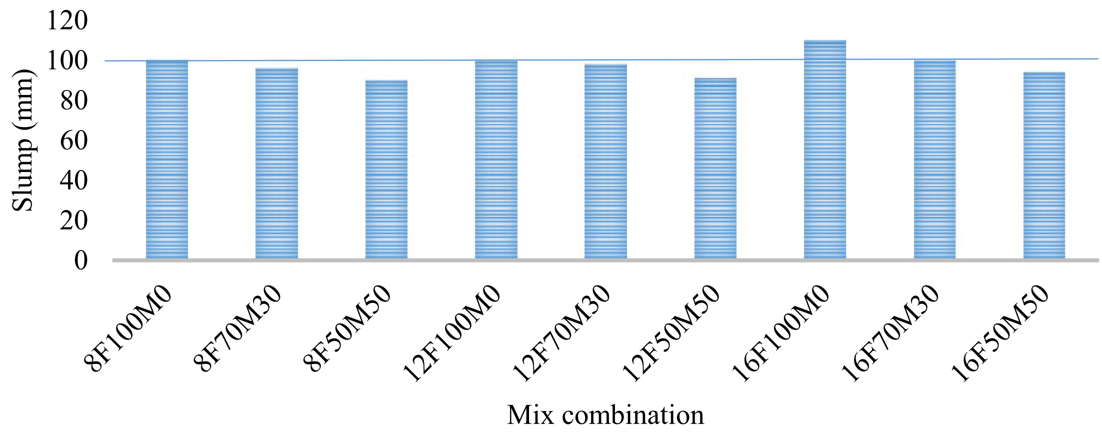

Figure 1. Workability of the GPC mixes

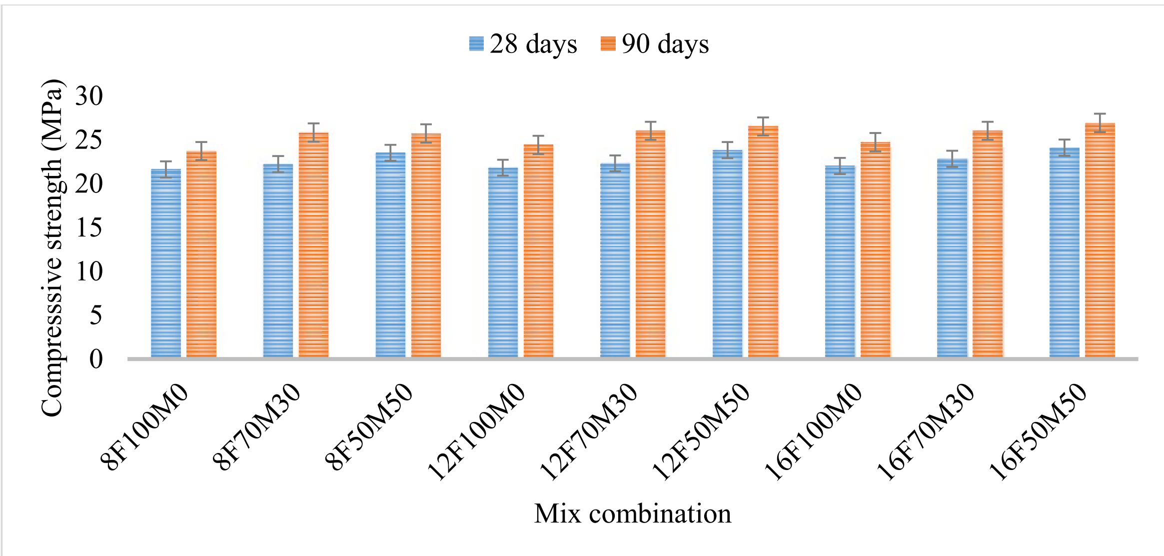

Figure 2. Compressive strength of the GPC mixes

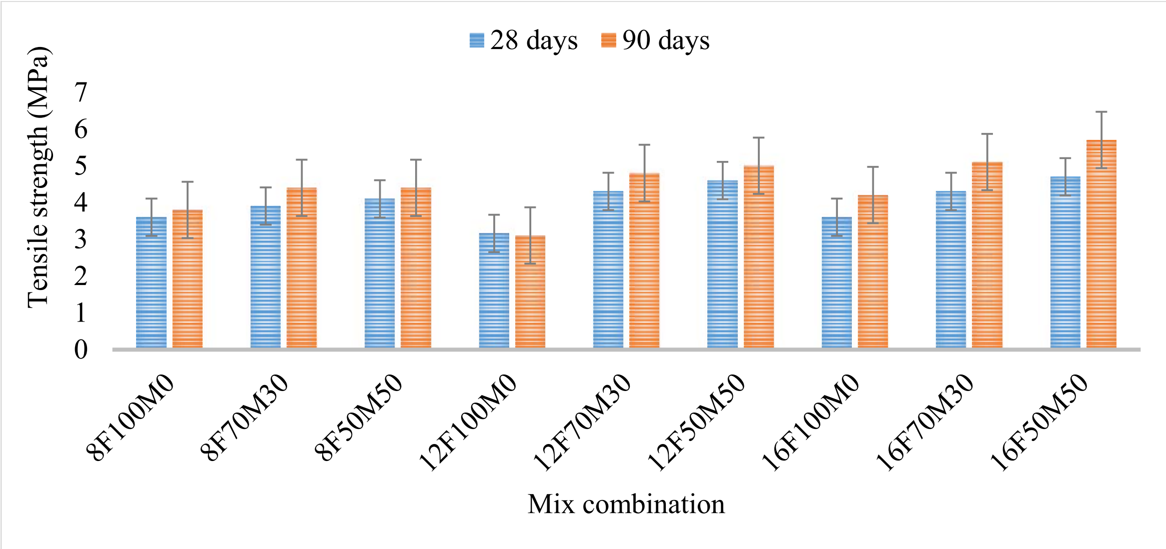

Figure 3. Tensile strength of the GPC mixes

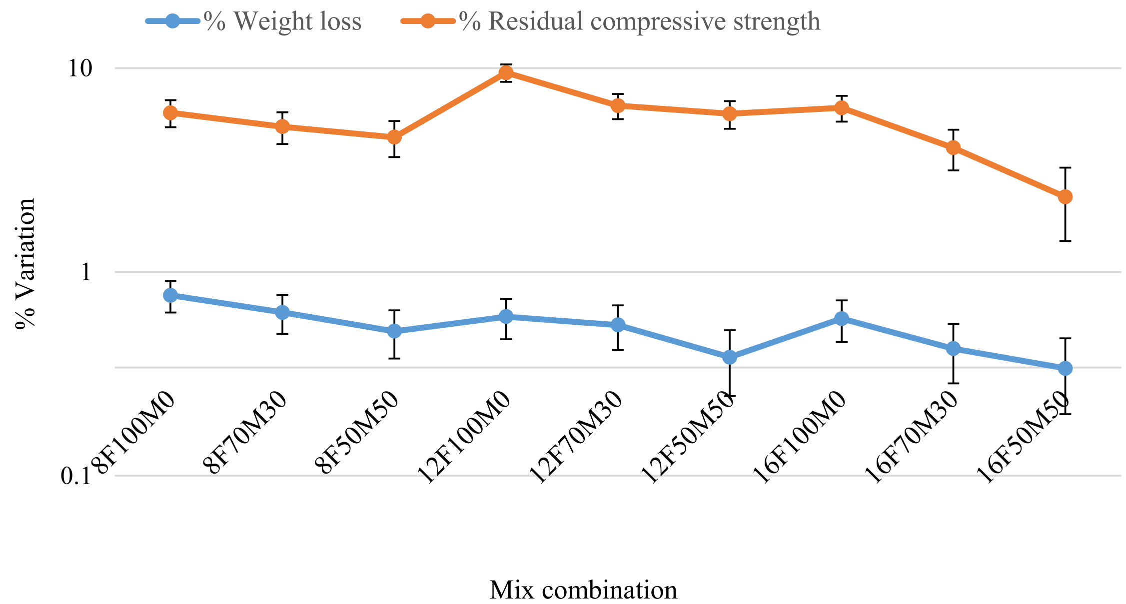

Figure 4. Percentage variation in weight loss and residual compressive strength after acid attack

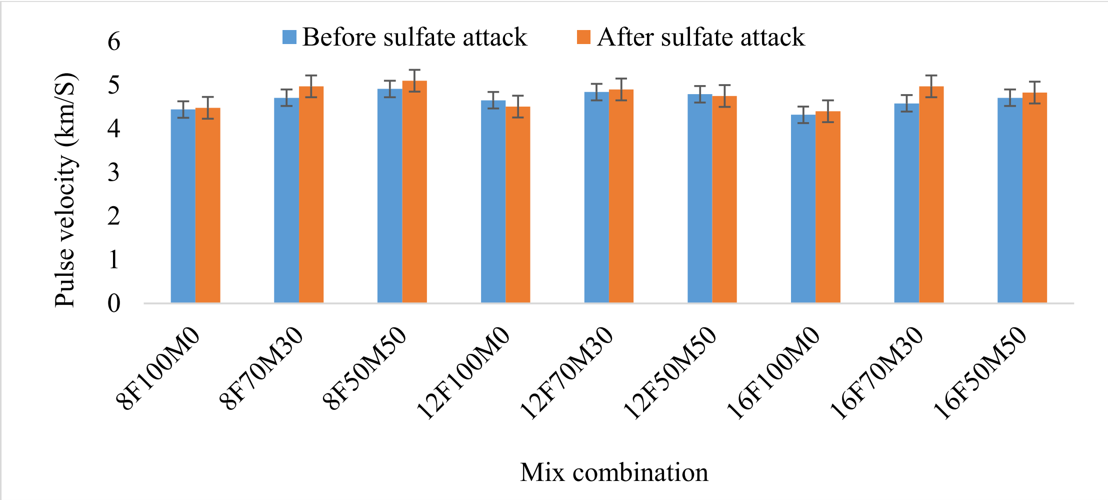

Figure 5. Comparison of the Ultrasonic pulse velocity of the GPC mixes before and after acid attack

4. Conclusion

A broad conclusion was drawn from the investigation and are enlisted as follows.

- The slump values were reduced with increasing metakaolin (% content) and concentration of NaOH compare to the control mix i.e. 100% FA based GPC with 8M. Maximum value was recorded at mix 16M, FA 50% and MK 50%.
- 50% replacement of FA with MK improves the compressive by 10-12% for 28 days curing age for 8M, 12M and 16M compared to control mix. Similarly, 28-34% enhancement in tensile strength was observed for 16M, FA 50% and MK 50% compared to control mix for 28 days.
- Percentage residual compressive strength were found to be very less for mix 16M, 50% FA and 50% MK i.e. 2.38% and maximum of about 9% for 12M, 100%FA for 28 days exposure to acid solution. The percentage loss in weight was observed to have minimum for 50% substitution of FA by MK with 16M and the maximum loss in weight was recorded for 100% FA with 8M.
- The average pulse velocity (km/s) for specimens of GPC mixes before and after acid exposure were measured between 4.91 – 5.1 km/s and 4.44 – 4.90 km/s respectively which means the porosity of the GPC specimens before exposure to acid was low and less permeable compare to later condition.
- Thus, metakaolin have positive impact on low calcium FA based GPC in improving the mechanical as well as resistance to chemical ingress in the GPC making the concrete more durable.

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