International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 14 (2018) pp. 11466-11470

Metakaolin Geopolymer Composite Concrete with High Durability

A. R. R. Kalaiyarrasi* P. PartheebanV. Muthupandi*****

*****Associate Professor, St. Peter's Institute of Higher Education and Research, Chennai, Tamilnadu, India.*

***Professor, St. Peter's College of Engineering and technology, Chennai, Tamilnadu, India.*

****PG student, Deakin University, Geelong Victoria, Australia.*

Abstract

Flyash (FA) is the commonly used alumino silicate raw material in Geopolymer(GP) synthesis. The porosity of FA-GP is mitigated in metakaolin (MK) modified Geopolymer. MK is also an alumino silicate rich material which is relatively pure and has a huge potential as Geopolymer precursor. Kaolin is abundant in India [1] and 4.48 million metric tonnes was produced in 2015. In this research FA is replaced with MK in 0, 25, 50, 75 % by mass. The smaller particle size and a high specific area of MK (3.5µm-1.5µm, 20 m^2/g) in comparison to flyash (10.05m^2/g) is taken advantage of in this research. The compressive strength of MK75 in 28 days has increased by 62% and by 16% in 120 days compared to MK0.The reduction of the volume of permeable voids percentage (VPV) to 0.638 for MK 75 compared to 18.58 for MK0 confirms that MK modified Geopolymer is strong and highly durable. The Scanning Electron Microscopy(SEM) and Electron Dispersive Spectrum(EDS) analysis supplement the experimental investigation.

Keywords: Metakaolin; Flyash; Geopolymer concrete; Compressive Strength; Durability, Ambient curing

INTRODUCTION

Cement is a widely used construction material due to its strength, durability and ease of mixing and placing. China, India and United States are the top 3 cement- producing countries. It is estimated that 1 tonne of cement during production releases approximately, 1 tonne of CO_2 into the atmosphere[2]. 6 % of the total CO_2 emission is from the cement industry. In an effort to reduce the usage of cement, geopolymer was synthesized by Joseph Davidovits [3] in1970 as an alternate to cement concrete. Geopolymerisation involves a chemical reaction between an alumino silicate raw powder and alkali metal silicate solution yielding amorphous to semi crystalline 3D polymer structures consisting of Si-O-Al bonds [4]. Fly ash (class F) used in geopolymer concrete is an alumino silicate powder derived as a waste from combustion of coal in thermal power station. Disposal of flyash is a serious problem which requires attention. Flyash based geopolymer concrete is porous and it influences the leechability, permeability and durability of the materials. Flyash geopolymers exhibit poor performance under adverse conditions.MK is obtained by calcining kaolin (china clay) at a temperature range of 500° - 800°C. Meta stands for the de-hydroxylation undergone by kaolin. Metakaolin conforms to ASTMC 618, class N pozzolan [5] specification.

When MK is used with ordinary Portland cement, on reaction with $Ca(OH)_2$ produces additional CSH gel. In MK modified geopolymer concrete it forms Si-O-Al bonds very rapidly. The high reactivity of MK is due to the thermal history, specific surface area and the particle size [6]. MK is calcined and has a specific surface area of 20 m^2/g (flyash 10.5m^2/g) and average particle size of 3.5-1.5µm. The resulting metakaolin modified geopolymer is stronger, denser and hence durable. This research attempts to investigate the mechanical and micromechanical properties of MK modified geopolymer concrete as a replacement for flyash in 25%, 50%, 75% percentages to utilize the advantages of MK precursor. 100% replacement is not done to avoid shrinkage cracks.

EXPERIMENTAL WORKS

Materials

Metakaolin geopolymer composite is composed of flyash and metakaolin as cementitious materials. Class F flyash used in this investigation is from Ennore Thermal power station, Chennai, India and Metakaolin is procured under the brand name Metacem from 20 Microns, Mumbai.

Table 1 Physical and Chemical composition of FA and MK

Chemical	Metakaolin	Flyash
SiO_2	58.90	48.0
Al_2O_3	37.23	29.0
Fe_2O_3	1.70	12.7
TiO_2	0.42	-
CaO	0.29	1.76
MgO	0.20	0.89
Na_2O	0.23	0.39
K_2O	0.26	0.55
SO_3	-	0.5
Loss on ignition	< 1	1.61
Physical property		
Specific gravity	2.5	2.06
Specific surface area m^2/g	19-20	10.5

Kaolin is sourced from the mines of Gujarat. The Physical and Chemical properties of FA and MK are given in Table 1. Aggregates used in this investigation are natural sand and crushed granite conforming to IS 383- 1970[7] Specifications for coarse and fine aggregates from natural sources for concrete.

Alkaline activator is a mix of Sodium Hydroxide and Sodium Silicate Solution. Sodium Hydroxide solution is prepared by dissolving 99% pure Sodium Hydroxide flakes in distilled water. Sodium silicate solution is viscid and conforms to IS 381 Indian Standard sodium silicate –Specification[8] with a composition of Na_2O (8.74 %), SiO_2 (27.96 %), H_2O (63.3 %) with the modulus of 3.2 (mass of Na_2O/ SiO_2=3.2). The ratio between two liquids was maintained as 2.5.

Figure.1 Constituents of MK geopolymer composite

Electron Dispersive Spectroscopy (EDS) analysis was performed to find the elemental composition of FA and MK [9]. Bands achieved at the various energy levels for FA are graphically represented in Figure 2. Peak achieved at 1.486 indicates the presence of Al atoms and peak at 1.739 indicates Si atoms. FA shows the presence of Ca, Fe and Ti. The mass composition of Si/Al of FA is 1.762 as given by Table 2.

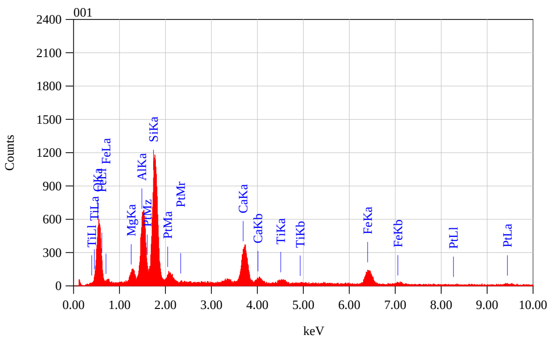

Figure. 2 EDS for flyash

As FA is a waste collected after burning coal used for thermal power generation, the composition and purity depends on the type of coal burnt and the location in the chimney from where FA is collected. Loss on Ignition of FA is 1.61, indicates the presence of unburnt coal particles. FA particles are spherical in shape and help in blending with other materials.

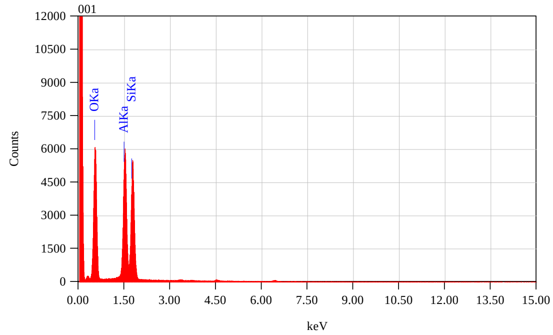

Figure. 3 EDS for Metakaolin

MK used in this study conforms to ASTM C 618 class N pozzolan and IS 1344-1981 Specifications for calcined clay pozzolan. MK satisfy the requirements of IS 1344-1981, [10] Specification for calcined clay pozzolan with the mass of

Table 2. EDS for Flyash

Element	keV	Mass%	Counts	Error%	Atom%	Cation K
O K	0.525	11.85	2722.37	0.01	24.09	1.3028
Mg K	1.253	2.93	929.51	0.09	3.92	0.9446
Al K	1.486	**13.96**	4241.90	0.02	16.83	0.9854
Si K* (Ref.)	1.739	**24.60**	7362.32	0.01	28.49	1.0000
Ca K	3.690	16.74	3210.01	0.03	13.59	1.5611
Ti K	4.508	2.21	332.97	0.29	1.50	1.9909
Fe K	6.398	16.74	1633.37	0.06	9.75	3.0674
Pt M*	2.048	10.96	799.19	0.15	1.83	4.1054
Total		100.00			100.00	

$SiO_2+Al_2O_3+Fe_2O_3$ not less than 70%, SiO_2 not less than 40%, and a fineness not less than 250-320 m^2 /Kg. The specific gravity of MK is 21.35% higher compared to FA, that would result in a slightly heavier material. Metakaolin is relatively pure with Si and Al atoms and other elements are in negligible quantity only.MK is light red in colour and the EDS analysis results are given in Table 3. In Figure 3, a small peak is observed at 6.398 indicating the presence of Fe element in small quantity which gives MK particular colour. The particle size of flyash is as high as D75 is 45µm and MK D5 is 45µm.

Table 3. EDS for MK

Element	keV	Mass%	Error%	Atom%	Compound Mass%
O K	0.525	53.30	3.67	66.29	62.0082
Al K	1.486	**21.17**	2.52	15.61	18.3560
Si K	1.739	**25.54**	3.26	18.09	19.6358

Methods

FA is replaced with MK in 25%, 50%, and 75% by mass in geopolymer concrete. Table 4 shows the quantity of materials required for $1m^3$ of GPC. The mix design [11] adopted for $1m^3$ of geopolymer concrete preparation. 400 grams of NaOH flakes was dissolved in 1 litre of distilled water to have 10 M NaOH solution. NaOH flakes were to be added to distilled water slowly and stirred from a distance, as the release of fumes and heat could cause discomfort. Sodium silicate solution was mixed with NaOH solution after 4-5 hours and stored in a container for its use in GPC. Alkaline activator was prepared 24 hours prior to its use in geopolymer concrete. Aggregates, flyash and Metakaolin were mixed thoroughly in a dry state in pan mixer of 40 litre capacity. Alkali activator was added and mixed for 5 minutes. The resulting geopolymer mix was cohesive and placed in the cube moulds of side 150 mm in three layers and compacted with tamping rod of 40 cm length.

Table 4. Mix Proportion

Mix	FA(kg)	MK (kg)	Sand(kg)	Coarse aggregate (kg)	AA (kg)
MK0	368	-	612	1346	184
MK25	276	92	612	1346	184
MK50	184	184	612	1346	184
MK75	92	276	612	1346	184

48 number of cube specimens of side 150 mm for compressive strength test, 48 number of Prism specimens of size 150 mm ×150 mm ×500 mm for flexural strength test, 48 number of cylinder specimens of 150 mm diameter and 300 mm height for split tensile strength and 12 numbers of 100 mm diameter and 50 mm thick cylinders for water absorption (WA) and VPV test by ASTM method.

Hydration of cement concrete requires water curing for strength gain, geopolymer gains strength by expelling water. In this investigation, ambient curing has been adopted to bring down the energy involved in geopolymer synthesis and for investigation of the suitability for practical in situ applications. Moulds containing the specimens are left at room temperature for two days and then demoulded. UTM of 1000 KN capacity is used for testing and tests were conducted in accordance with IS 516-1959[12]. Geopolymer concrete cylinders of 100 mm diameter and 50 mm thick of MK0, MK25, MK50, MK75 mix at 28 days were tested for porosity in accordance with ASTM C642-06 Standard Test Method for Density Absorption and Voids in Hardened Concrete[13]. The mass of the cylinders in dry condition was measured and noted as A. Cylinders were immersed in water for 24 hours and mass was determined as B after wiping the surface water with a towel. Cylinders were boiled in tap water for 5 hours and cooled naturally for 14 hours to a temperature of 20-25 °C. Surface moisture was removed from the cylinders and mass was noted as C. After immersion and boiling the cylinders were suspended in water by means of a wire and the apparent mass is noted as D. ASTM 642-06 is adopted for determining the density, percentage of WA and percentage of VPV in geopolymer concrete.

5 cm×5 cm ×1 cm broken piece of hardened geopolymer cube specimen each of MK0, MK25, MK50, MK75 at the age of 28 days was collected. It was stored in acetone till the day of testing. Storing of specimens in acetone arrests further geopolymerisation. The samples are oven dried before testing. Thin Platinum coating was given to the specimen to make it conductive. Magnifications were varied from 250 to 4000 to observe the microstructure of geopolymer concrete.

RESULTS AND DISCUSSIONS

Compressive strength is the mandatory property based on which concrete is graded and recommended for structural use. Variations in compressive strength of MK modified GPC are presented in Figure 4. MK modified GPC of MK75 mix develops higher compressive strength of 21.5 N/mm^2 compared to 8.4 N/mm^2 for MK0 at the age of 14 days, 155% larger. At 28 days compressive strength of MK0 is 14 N/mm^2 and for MK75 is 22.7N/mm^2, 62% more. However, the compressive strength of MK0 and MK75 at 120days was 30.4 N/mm^2 and 35.3 N/mm^2 respectively, only 16% larger. The increase in the compressive strength of MK modified GPC for MK25, MK50, MK75 mix is 0%, 8.4%, 16.11% at the end of 120 days. EDS analysis of MK metakaolin showed the Si/Al mass ratio as 1.21, and Si/Al mass ratio of flyash as 1.762. When MK is compared to FA, for lesser Si/Al ratio the compressive strength increases. This demonstrates the advantage of the particle shape and size of metakaolin over flyash.

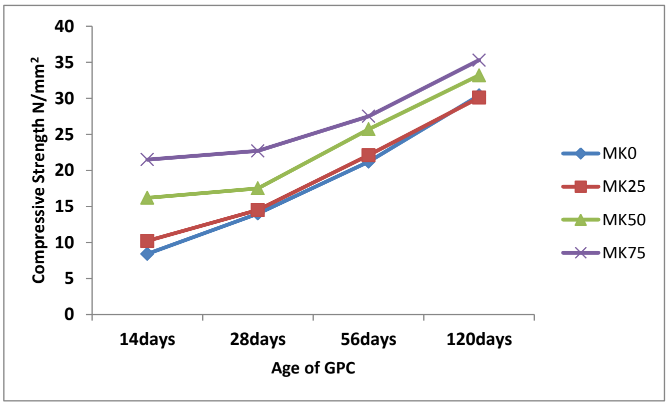

Figure 4. Compressive strength

The gain in split tensile strength in the case of MK was very quick as in the case of compressive strength. At the end of 120 days, the gain in split tensile strength of MK25, MK50, MK75 mix of MK modified GPC follows a pattern similar to that of gain in compressive strength of MK modified GPC. The gain in split tensile strength of MK25 at the end of 120 days is 1% and in MK50 mix the gain in split tensile strength is 11.11%. The gain in split tensile strength of MK75 of MK modified GPC is 18.18% compared to MK0.

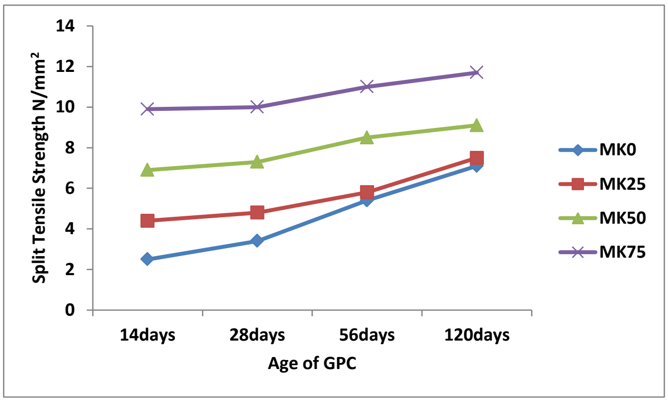

Figure 5. Split Tensile Strength

Flexural strength of MK modified GPC varies in order with compressive strength variations and is presented in Figure 6. The rate of increase of flexural strength between 28 days and 56 days is 28% and 25% between 56 days and 120 days for the M25 mix of MK modified GPC. The rate of increase of flexural strength between 28days and 56 days was 50.9% and between 56 days and 120 days is 12.3% for MK50 mix of MK modified GPC.

The performance of concrete in adverse conditions is well understood from the porosity of the concrete. The durability of MK modified Geopolymer was established by reduced WA percentage and percentage VPV of MK modified GPC compared to FA GPC. Water absorption of FA geopolymer is 7.5% and that of MK modified Geopolymer (MK75) is 0.2%. Figure 7 presents the variations in water absorption with the type of mix. Water absorption of GPC reduced with the increase in the percentage of MK precursor.

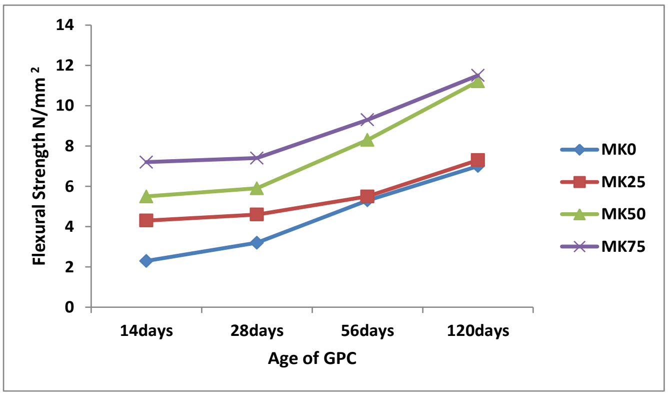

Figure 6. Flexural Strength

MK modified GPC presents a homogenised structure compared to FA modified GPC. Dry density slightly increased from 2.06 for MK0 to 2.49 for MK75. VPV reduced from 18.48% for MK0 to 0.63% for MK 75. Decrease in the porosity of metakaolin modified GPC is due to the geopolymerisation structure. Flyash based geopolymer is crystalline in nature as it is evident from SEM image presented in Fig.8. Metakaolin modified geopolymers geopolymerises to a homogeneous structure as deduced from Fig.8. Though the strength aspect of the GPC is dependent on the Si and Al content of the raw material, the porosity values depends on the microstructure of GPC.Geopolymerisation of metakaolin modified geopolymer is better understood using microstructural investigation using SEM and EDS. The microstructural investigations agree with the experimental investigations of metakaolin modified geopolymer concrete.

Table 5. EDS analysis at 002 on MK 50

Element	(keV)	Mass	Error	Atom	Cation
O K	0.525	56.88	3.03	68.51	60.1018
Na K*	1.041	12.52	3.32	10.49	7.6937
Si K*	1.739	30.6	2.56	21.00	32.2046

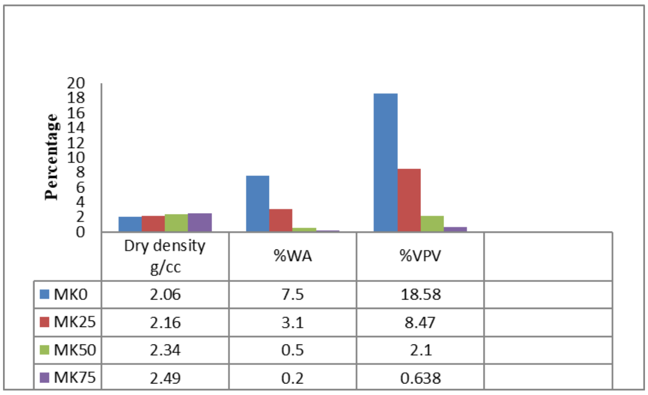

Figure 7. Dry density, % WA, %VPV

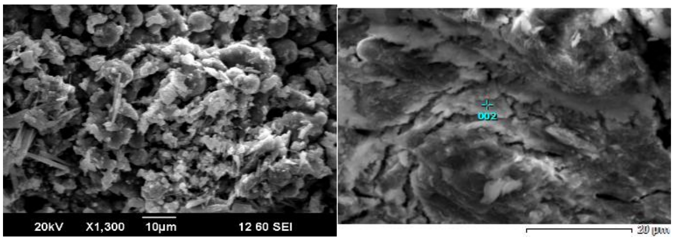

Figure 8. SEM image of MK0 & MK50

EDS Analysis was done to understand the geopolymerisation of the concrete. MK50 mix was chosen for investigation. Table 5 presents the EDS analysis done at 002 spot of the MK modified GPC. The absence of Al in the matrix indicates the Si-O-Si bonds which is the result of a higher degree of geopolymerisation,resulting in Polysialate Disilaxo[6]. Figure 9 presents the EDS analysis of spot 002 of MK modified GPC.

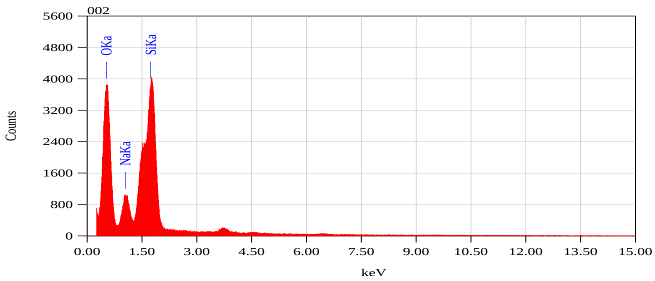

Figure.9 EDS analysis at 002 of MK50

CONCLUSION

- The main hindrance in the practical application of GPC is that it has to be cured under elevated temperature. It is possible to synthesize MK modified GPC in ambient curing. MK75 mix of MK modified GPC gains a compressive strength of 22.7 N/mm^2 at 28 days.
- The rate of gain in strength is more in MK included GPC compared to FA- GPC (MK0). MK-GPC can be used in places where higher initial strength is required.
- The durability of MK modified Geopolymer was established by reduced water absorption percentage and percentage volume of permeable voids of MK.
- The cost involved in MK modified Geopolymer is twice as that of cement concrete of equal strength. Novel methods of producing MK may bring down the cost.
- As cement is totally avoided, there is 80%. saving in CO_2 emission.

REFERENCES

[1] Indian Minerals Year Book (2013) Part III, Ministry of Mines, Government of India.

[2] Davidovits, J. “Pyramid Illusions, A journey to the truth”, Basket Publishing, ISBN 0-9652509-7-0, 1996.

[3] Davidovits, J. “Le Livre de la Pierre, Que le Dieu Khnoum Protégé Kheops, Consteur de Pyramide, ISBN 2-902933-02-9,1978.

[4] Davidovits J. (1982) Minerals polymers and methods of making them. US 396, Patent4472199.

[5] ASTM (2015) American Standards for Tests and Measures ASTM C 618-15, Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete, ASTM International, West Conshohocken, Pennsylvania , USA.

[6] Davidovits. J. (1991) Geopolymers: inorganic polymeric new materials. Journal of Thermal Analysis. 37:1633–56.

[7] Indian standard specification for coarse and fine aggregate from natural sources for concrete: IS 383-1970, Bureau of Indian Standards, New Delhi, India.

[8] IS 381 (1995) Indian standard code for sodium silicate specification: Bureau of Indian Standards, New Delhi, India.

[9] Kalaiyarrasi, A. R. R. and Partheeban, P. “Influence of Si/Al ratio on the compressive strength of metakaolin based geopolymers”, International Journal of Earth sciences and Engineering, Vol. 9, pp. 87-91, 2016.

[10] Indian standard code for specification of calcined clay pozzolona: IS 1344-1981, Bureau of Indian Standards, New Delhi, India.

[11] Lloyd, N. A. and Rangan, B. V. “Geopolymer Concrete with Fly Ash”, Second International Conference on Sustainable Construction Material and Technologies, Universita Politechnica delle Marche, Ancona, Italy, June 28-30, 2010.

[12] Indian standard code for method of tests for strength of concrete: IS 516-1959, Bureau of Indian Standards, New Delhi, India.

[13] ASTMC 642-06 Standard Test Method for Density, Absorption, and Voids in Hardened Concrete. ASTM International, 100 Barr Harbor Drive, P.O. box C-700 West Conshohocken, Pennsylvania 19428-2959, United States.