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Application of Response Surface Methodology: Optimum Mix Design of Fly ash geopolymer mortar, a Portland cement free binder for sustainable construction.

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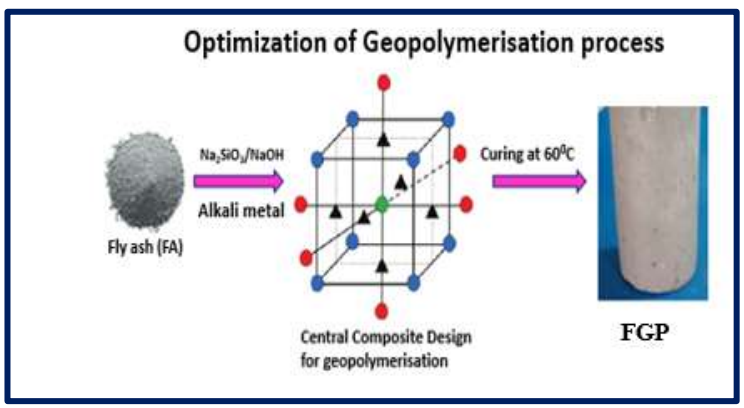
Abstract : Geopolymers are inorganic polymers fashioned from the alkaline activation of amorphous alumino-silicate substances ensuing in a 3-dimensional polymeric community. Geopolymerisation is an innovative technology that may remodel several aluminosilicate materials into beneficial products and programs are infinite: creation and infrastructure industry, ceramics and poisonous metals containment and plenty greater. However due to the variability in the raw substances chemical composition, reactivity, activator kind and concentrations, reaction (curing) time and temperature, the product properties various widely. Hence optimization of system parameters necessitated for the excellent control of products in big scale up production. To clear up the optimization trouble of parameters and situations in fly ash geopolymer instruction correctly, a sequence of studies, experiments were designed and carried out the usage of response surface method (RSM). Firstly, Single component gradient analysis changed into adopted to decide the reasonable degree of various factors inside the reaction surface evaluation and 28-day compressive electricity development has been fixed as target performance parameter which rely upon response manage parameter together with sodium silicate modulus, NaOH content, water /fly ash ratio, silica content, curing temperature and curing time. Secondly, the practice situations were optimized to enhance the 28-day compressive power of the substances based at the imperative composite layout and high strength geopolymer materials became prepared through this technique. The study also proved the effectiveness of RSM to optimize the training situations of geopolyme
Keywords : Geopolymer, Fly ash, compressive strength, Response surface methodology(RSM).

Graphical abstract:



1.0 Introduction:

Cement plays an important role in construction and national economic development and it also considered as second to the fresh water as the most widely used commodity [1,2] However, the environmental footprint and energy intensity associated with these cement-based materials have been recognized as an alarming issue toward the development of sustainable infrastructure in a carbon-constrained society. About two billion tonnes of CO2 emitted every year from cement manufacturing process per year (which is around5-7% of the global anthropogenic CO2 emission) including emissions of harmful particulates (3-5). In search for Cement less alternative binder which opens an opportunity for the development of the alkali activated materials. Geopolymers, a subset of alkali activated materials [4,6,7] are systems of inorganic binders proposed by Prof Davidovits during 1970's [8]. These alumino-silicates are formed by activating alumino silicate powder precursor materials with an alkaline hydroxide or silicate solutions. The precursors can come from a range of sources with various ratios of aluminium (Al) and silicon (Si) that include natural minerals (clays), calcined clays (meta-kaolin), biomass, industrial by products viz: fly ash, GGBS, Copper slag, red mud, rice husk ash etc.,

Many geopolymer formulations have been investigated and shown to have comparable if not better technical properties than OPC .The chemistry of geopolymeric reaction and rate of strength development of geopolymeric mortar (product) are influenced by several factors based on the chemical type and composition of precursor raw materials , alkaline activators, water content, type of aggregates, blending components and processing conditions that affect the geopolymer reactions and present different mechanical properties and microstructures [9].Several studies have been conducted to investigate fly ash based geopolymer concrete properties. [10] The results indicate that fly ash based geopolymer has significant resistance to acid and sulfate attack, high early compressive strength and good performance at high temperatures. It has also been projected that geopolymers can be formulated for specific niche applications [5,11-12]. Hence it is understood that the processing requirements can be managed to produce the desired fly ash based geopolymer characteristics in the most practicable means possible.

In this study, to explore the potential of the sustainable waste utilization of Fly ashes in the geopolymerisation reaction were evaluated after chemical characterization and fly ash reactivity. The optimization of reaction conditions using Response surface methodology (RSM), a experimental design method by maximizing the overall desirability of the geopolymer products has been reported [13]. RSM has advantages of a relatively small number of test groups, reducing costs, improving efficiency and so on, it is widely used in biological, chemical, machinery, agriculture, etc.. But the application of RSM is unusual in the field of civil engineering particularly in the research of building materials preparation conditions [14,15]

2. Materials and Test Methods:

2.1 Raw Materials:

The Geopolymeric source material(GSM), Class F fly ash sample were collected from the thermal power plant, Gummidipoondi, India. The chemical composition of the source material was analyzed using EDXRF techniques presented in Table.1. Alkali solution used in the study was the combination of sodium silicate solution (Si/Al 2.2., 15% Na2O, 33% SiO2 and 52% H2O) and lye (50% NaOH). The final molar ratio of SiO2/Na2O=1.1.

Table.1 Chemical composition of Fly ash.

Components	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	CaO	MgO	K_2O
Fly ash	47.5	33.4	10.1	0.01	2.09	0.1	1.6

2.2 Response Surface Method (RSM):

Response surface methodology (RSM) is a combination of mathematical and statistical techniques used for the development, improvement, and optimization processes [17]. RSM has been a powerful tool for the process evaluation and optimization dominantly in the industries but also presents strong applications in the

research sectors to predict the results when they are function of controlled independent variables. The fundamental equation as given in eqn (1) the response(Y) which is a dependent variable like £i, £2.. (independent variables) and £k as well the error E.

$Y = f\ (£_1, £_2 \ldots\ldots £_k) + £$ (1)

Where ' Y ' is the response of the experiment which is the function of various independent controllable variables and £ is the representation of other uncontrollable sources of variations for the outcome y. The controllable variables as shown in the Equation 1 are in the natural form with their respective physical units that are difficult to handle. Hence these variable are converted into coded variables $x_1, x_2, \ldots x_k$ having zero mean value with same standard deviations can be represented ineqn(2)

$\eta = f\ (x_1, x_2 \ldots\ldots x_k)$ (2)

The response surface is planar when the interaction term is zero/negligible. The linear model is not sufficient to represent the experimental data adequately, because most of the parameters are inter dependent .Hence the Central Composite Design (CCD) has been considered and resolved by the quadratic equation in addition to those of factorial design. It consists of three parts namely Factorial(Cubic), axial and Centre point interaction. The response surface using CCD technique by the quadratic response surface as given in the Eqn (3)

$$y = \beta_0 + \sum_i \beta_i x_i + \sum_i \beta_{ii} x_i^2 + \sum_{i<j} \sum_j \beta_{ij} x_i x_j + \varepsilon. \qquad (3)$$

In our present study, the three individual desirability function that are dependent on the values of the response variables Yi , consider as performance characteristics strength of geopolymer. The process conditions are considered as independent variables, they are : Molar ratio of sodium silicate as ' S'; Molarity of NaOH as ' H' and R is the AS/binder.

$Y_i = f\ (S,H,R)$ (4)

Based on central composite design fifteen set experiments were generated based on the equation(5).

$N = 2n+2n + 1$ (5)

where, N is the required experimental points, n is the number of input parameters for each

experimental point. In our case n = 3 and, hence the required number of experimental points is N= 15.

Therefore, in this case using k = 3 ,we can expand the above equation(4) we get equation (6) .

$\eta = \beta 0 + \beta_1 S_1 + \beta_2 H_2 + \beta_3 R_3 + \beta_{11} S_{12} + \beta_{22} H_{22} + \beta_{33} R_{32} + \beta_{12} S_1 H_1 + \beta_{13} S_1 R_1 + \beta_{23} H_1 R_1$ (6)

The performance of the different factors was evaluated independently using the runs randomly ordered by Design Expert software for Response Surface method. Considering the factors in Table 2, the Response Surface Methodology(RSM) of Central Composite Design generated fifteen sets of designed experiments that was used for the evaluation.

2.3 Mix Design:

Geopolymer mortar samples were prepared by mixing the fly ash and aggregate as a dry mix thoroughly for 2 mins in the Digi mortar mixer machine. The liquid to binder ratio 0.5 was fixed for all GP mortar samples and the mixing was continued for 8 mins for uniform mixing The mixing was continued for further 4 mins and the GP mortar were poured into pre-oiled mould. It was compactly packed by using vibrating table and casted into the cylindrical specimens of size 50mmX100mm. The samples were cured at ambient temperature and hot oven air curing at 60^0C. The mechanical test was carried out by compressive testing machine at 28 days. The synthesized Geopolymeric paste samples was used for further characterization studies

Table.2Central composite design for three coded factor level

Notations	Factors	Coded values				
		+1.63	**+1**	**0**	**-1**	**-1.63**
		Un coded values for factors				
S	Na_2SiO_3/ NaOH	2.4431	2.041	1.3	1.15	0.6
H	NaOH(M)	11.266	10.0	8.0	6.0	4.732
R	AS/Binder	0.75	0.63	0.55	0.4	0.35

2.4 Test Methods:

- X-ray diffraction(XRD) was carried out using Brucker instrument with XRD-Phillips pW 1710" (Cu Kα = 1.54178).
- Fourier transform infrared (FTIR) spectroscopy, using the KBr pellet method in a Bruker Tensor 27 spectrometer, scanning 32 times from 4000 to 400 cm-1 at 4 cm-1 resolution.
- Field Emission Electron Microscopy(FESEM) was conducted using JEOL JSM 6300 microscope with a tungsten filament electron source, and 20 kV accelerating voltage. The samples were evaluated in low vacuum mode. X-ray spectrometer system (energy dispersive spectroscopy (EDS)) was used to determine the chemical compositions of the phases identified.
- Malvern Zetasizer (Nano series) was used to measure the zeta potential with 0.5 weight % of Geopolymer paste in deionized water against the standard potassium tungsto -silicate solution and calculations were made through Zetasizer software.

3. Results and Discussion:

3.1 Response Surface Optimization:

The experimental trials were made per the suggested input from RSM. The resulted compressive strength of different mixes has been made as a put for further analysis. The regression coefficient obtained for the experimental design along with their corresponding T and P values are tabulated and as shown in Table 3.

The p-value is of <0.05 showing high significance of all the input parameters and it was considered for the construction of the RS model. The resulted regression model obtained with R-squared value of 95.56% and s-value of 8.02. as well the coefficients of determination (R-squared) are very near to 1.0, indicating the best fit data to the model assumed.

Table.3 Regression co-efficient for the RSM model.

Coefficients	Coef(Coded)	SE Coef. (Coded)	T-value	P-value
Constant	2.2	12.8	0.17	0.00
NaOH(M)	2.14	1.15	1.86	0.01
Na2SiO3/NaOH	9.44	3.28	2.87	0.011
AS/Binder	-11.0	13.1	-0.84	0.001

3.2 Analysis of Variance:

Diagnostic plots are useful to see whether assumptions are met. Fig 1, shows the residual plot and regression diagram exhibiting the fits and the experimental observation for the attribute, The compressive strength. As observed there is no significant defections from the normal probability line and can be fairly conclude that the assumptions of normality is satisfied.

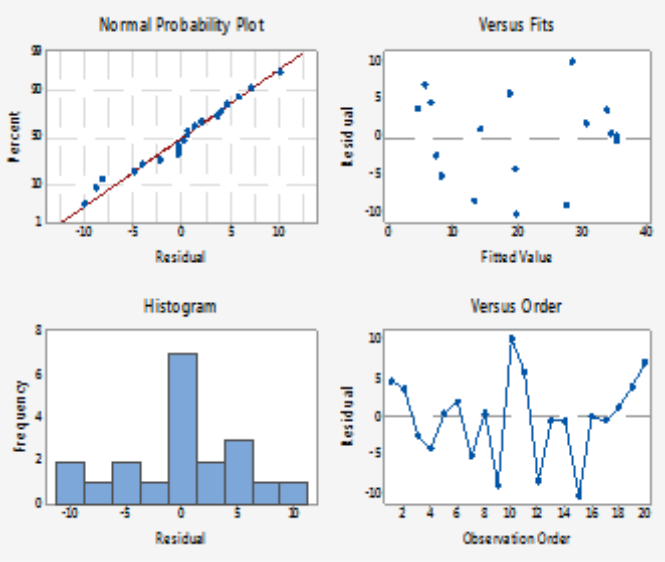


Fig.1 Residual plots for mechanical strength(Mpa) of GP mortar

The optimized process conditions obtained from RSM analysis for each variable has depicted in the scatter plot. (Fig .2) It was found that the order of influence is as S>R>H.The interaction between the variables depicted that SH is significant, HR is highly significant and interactive item SR is insignificant.

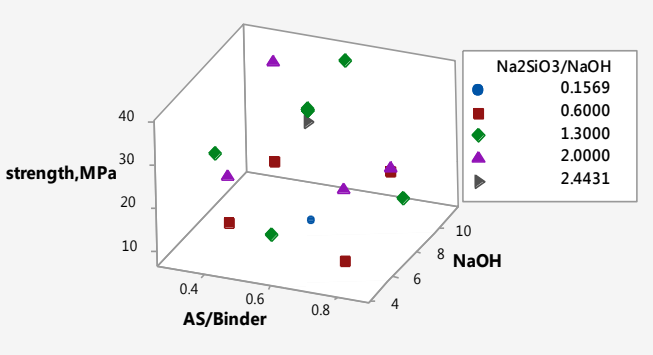


Fig .2 Scatter plot for the GP mortar

The degree of influence on compressive strength and interactions of factors were described in the Fig.3.The shape of 3D response surface and contour can reflect the degree of interactions. Fig 3(a) and (c) are steep and contour is circular. Fig 3 (b) is more of steep and elliptical as it represents signifiant interactions between the factors.

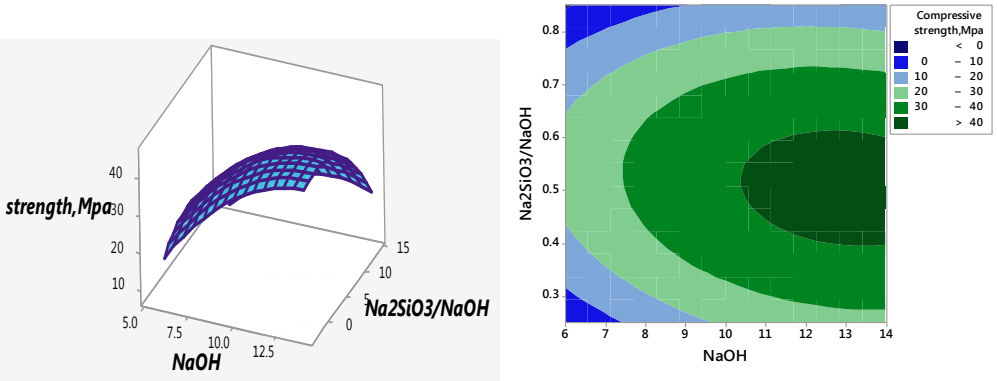


Fig.3(a) Surface and contour plots showing the relation between NaOH,Na_2SiO_3/NaOH and strength for AS/Binder=0.3

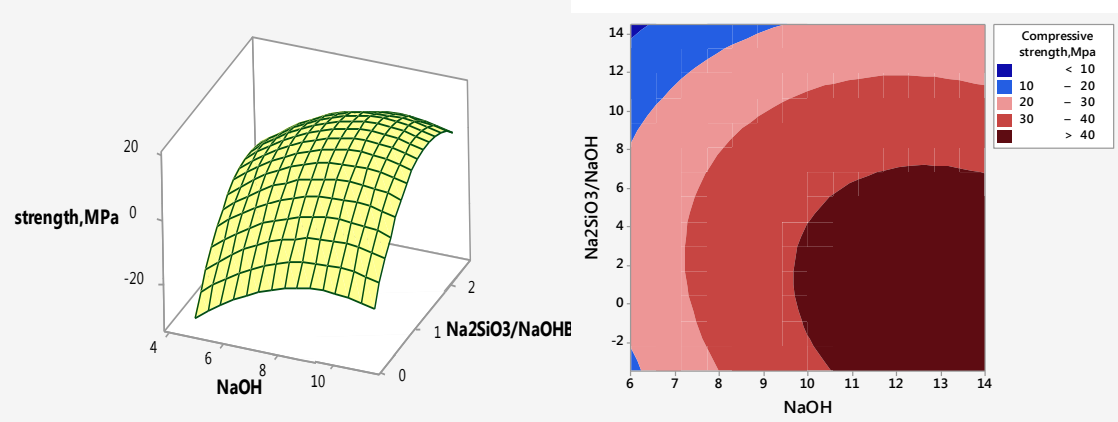


Fig 3 (b) Surface and contour plots showing the relation between NaOH,Na_2SiO_3/NaOH and strength for AS/Binder=0.5

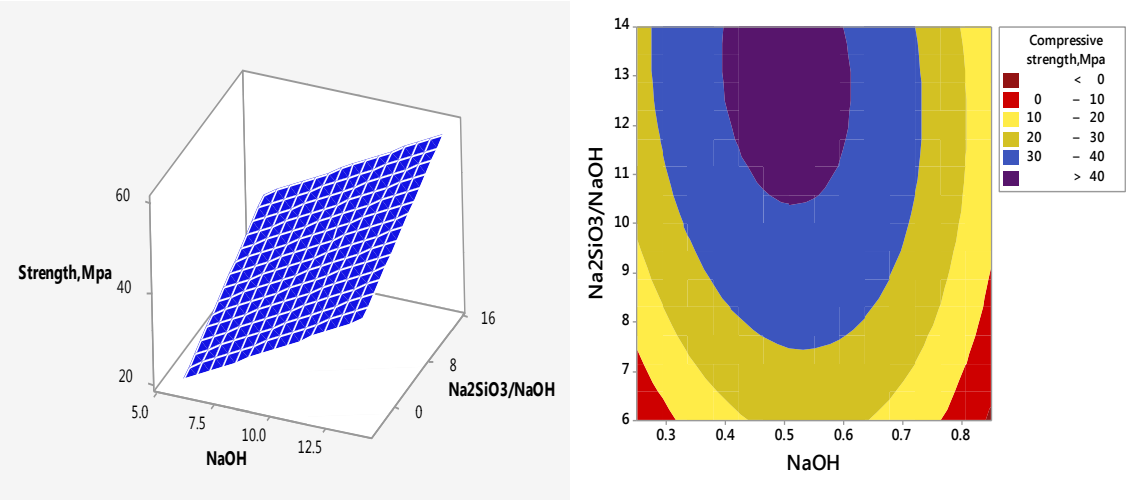


Fig 3 (c) Surface and contour plots showing the relation between NaOH, Na_2SiO_3/NaOH and strength for AS/Binder=0.75

3.3 Optimization of Process Conditions and Verification:

The validation of this model from the experimental observations were shown in Table.4. Based on the backward elimination approach for best fitted model predicted the following process parameters:

- NaOH :10 M
- Na_2SiO_3/NaOH: 1.3
- AS/Binder.0.55,
- curing temperature :60^0C
- Time: 24hr.

The strength obtained is in the range 25-30 Mpa.

Table.4 Validation of the developed RS regression model

Mix Id	NaOH	Na_2SiO_3 /NaOH	AS/Binder	Predicted strength MPa	Experimental Strength MPa	Error (%)
FG1	10	1.3	0.35	23.19	21.45±5	-8.14
FG2	8	1.0	0.4	11.41	12.54±3.4	9.63
FG3	8	1.3	0.55	22.36	35.12±4.5	36.09
FG4	6	0.6	0.63	8.4	10.395±2.8	-23.75
FG5	4.7	1.3	0.7	15.24	15.51±3.5	1.63

3.4 Microstructure Analysis of Fly Ash and FGP Mixes:

3.4.1 XRD For Fly Ash and FGP Mix:

The main phases formed in XRD pattern of the fly ash contains both amorphous or non-crystalline content. In a non-crystalline state, diffraction of X-rays resulted in a broad diffuse halo rather than sharp diffraction peaks. The broad peak of amorphous structure can be observed around 22° 2θ . Fig. 5, shows that the major mineral components of original fly ash samples were quartz (PDF#46-1045), Mullite (PDF#85-1460) and hematite (PDF#88-2359). The presence of the sharp peaks detected in the fly ash was due to the presence of quartz. The diffractogram for the original fly ash changed perceptibly when the fly ash was activated by alkaline solutions whose halo is attributed to the vitreous phase of the original ash slightly shifted from 25° to 40° 2θ values. This change indicates the formation of an alkaline aluminosilicate hydrate gel which has been identified as the primary reaction product and the characteristics diffraction patterns of geopolymeric [20-28].The most intense peak around $2\theta = 25^0$ was attributed to an amorphous silicate phase consisting of a SiO_4 tetrahedral sharing oxygen atoms[25]. The XRD analysis showed that the evolution phases geopolymer matrix play an important role for determining the interaction between fly ash particles and alkaline solution and they are only slightly different and not obvious.

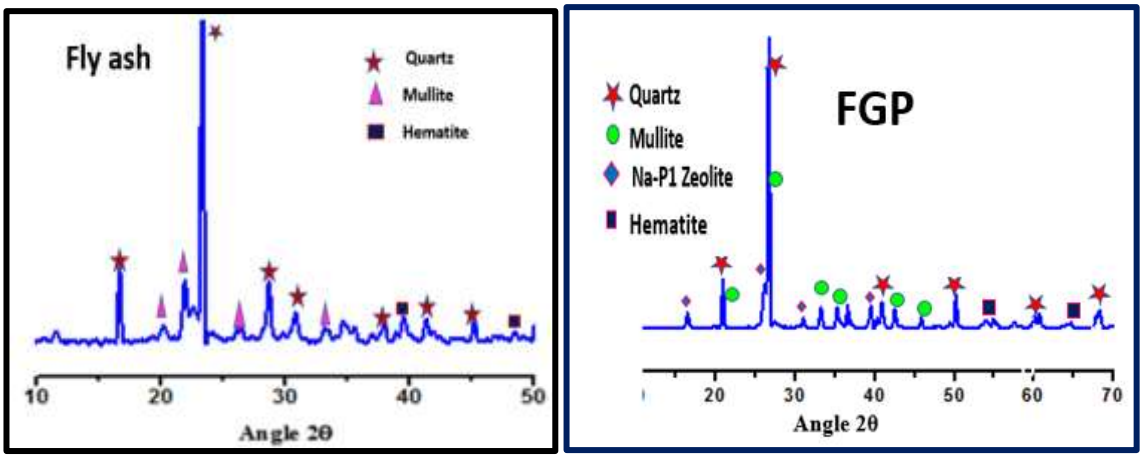


Fig 4. XRD pattern for Fly ash and FGP geopolymer mixes.

3.4.2.SEM Analysis:

During coal combustion process, the smooth spherical particle are formed as a result of thermochemical transformations of mineral particles where the minerals melt to form small droplets, which upon sudden cooling and action of surface tension forces adopt the spherical shape [29]. It can be seen that fly ash contains spherical particles with smooth outer surfaces from Fig 5. The synthesized geopolymer consists of agglomerated particles and partially broken sphere it is due to the dissolution of SiO_2 and Al_2O_3 (contained in the fly ash) in alkaline solution leading to the formation of aluminosilicate gel [30] which then acts as a precursor to geopolymer formation. In the micrograph, the presence of gel (sodium aluminosilicatehydrate(N-A-S-H gel) that forms the cementitious matrix could be observed alongside the spheres of unreacted ash particles [20] is observed in the Fig .5.

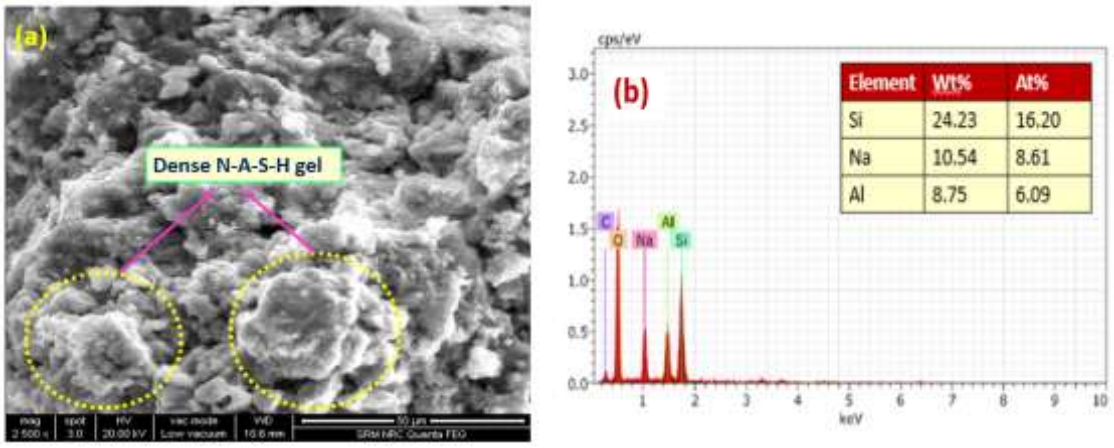


Fig 5. FESEM of a) FGP geopolymermixes b)EDAX of FGP.

3.5 BONDING NATURE BY FT-IR:

The precursor material fly ash (Figure 5)contains a sharp band around1071 cm^{-1} is due to the asymmetric stretching of (Si, Al IV)-O-Si in glass and partially overlapped by phases of mullite and quartz. The vibrational frequency at 904 cm-1(m) which corresponds to the asymmetric stretching of (Si, Al IV)-O-Si in amorphous glasses which could be composed of higher Al concentration. The symmetric stretching of Si-O-Si in quartz and Al(IV), symmetric stretching of Al-O-Si in Mullite or Mullite like structure was found around 800 cm-1(w) and 558 cm-1(w) . These bonds are said to be 'inactive'. Generally, the inactive bond appears as weak but the active bonds are sharp. The vibrational frequency assignments of fly ash are tabulated in table.5

Table.5 Vibrational frequency assignment of FA

ν(cm-1)	Assignment	Nature
1071 (S)	Asymmetric stretching of (Si, Al IV)-O-Si in glass this is due to the partially overlapping of mullite and quartz.	Active
904 (m)	Stretching of Si-O-M where M - Alkali metal	Active
800 (w)	Symmetric stretching of Si-O-Si in quartz and AlVI	Inactive
558 (w)	symmetric stretching of Al-O-Si in mullite or mullite like structure	Inactive

The vibrational frequency around 1030cm^{-1} corresponding to the precursor material is shifted to 800-900cm^{-1} ,this is due to the penetration of Al^{4+} atoms into the initial -Si-O-Si- skeletal structures. This confirms the condensation of Si-O tedrahedran in geopolymer paste. Symmetric stretching vibrations of -Si-O-Si- and -Al-O-Si- can also be identified near 740 cm^{-1}, and bending vibration of -Si-O-Si- and -O-Si-O- in the 450 cm^{-1}regions.

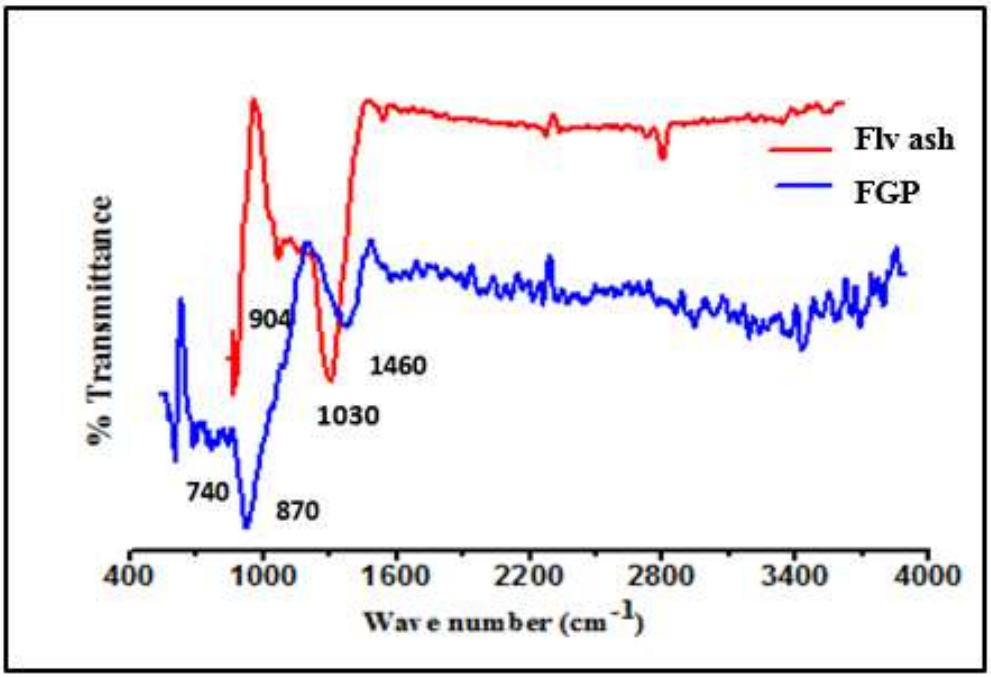


Fig 4. FT-IR for Fly ash and FGP geopolymer mixes.

Conclusion:

Fly ash geopolymerisation reaction having complex chemistry between the precursors and Activating solution property that has been performed from the RSM suggested experimental design. The experimental values of compressive strength for the optimized process conditions are strongly corroborated with the model predicted attributes. Hence the advancement of statistical tools is useful to minimize the number of trials and predict the target performance of the Geopolymer products at large scale preparation. The application of RSM is unusual in the field of civil engineering particularly in the research of building materials preparation conditions This study will extend to tailor made the Geopolymeric products for commercial applications.

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References:

1. Aitcin, P.C., (2000). “Cements of yesterday and today: concrete of tomorrow”. Cement and Concrete Research, 30, 1349–1359.
2. Akcay, B. andTasdemir, M. A., (2009).“Optimisation of using lightweight aggregates in mitigating autogenous deformation of concrete”.Construction and building materials, 23 (1), 353 – 363.
3. Damtoft,J.S., Lukasik,J., Herfort,D., Sorrentino,D., and Gartner,E.M., (2008). “Sustainable development and climate change initiatives.” Cement and Concrete Research, 38 (2), 115–127
4. Shi C., Jinénez, A.F., Palomo, A., (2011). “New cements for the 21st century: the pursuit of an alternative to Portland cement”. Cement and Concrete Research, 41, 750 – 763.
5. Ogunkunle, C.O. and Fatoba, P.O., (2013). “Pollution loads and the ecological risk assessment of soil heavy metals around a Mega Cement Factory in Southwest Nigeria”.Pollution Journal of Environmental Study, 22, (2), 487 – 493.
6. Juenger, M.C.G.; Winnefeld, F.; Provis, J.L.; Ideker, J.H. Advances in alternative cementitious binders. Cem. Concr. Res. 2011, 1, 1232–1243.
7. Suhendro, B. Toward green concrete for better sustainable environment. Procedia Eng. 2014, 95, 305–320.

8. Van Deventer, J.S.J.; Provis, J.L.; Duxson, P. Technical and commercial progress in the adoption of geopolymercement. Miner. Eng. 2012, 29, 89–104.
9. Joseph Davidovits, Geopolymer Chemistry and applications Book, Geopolymer Institute,2008.
10. Fernández-Jiménez A, Palomo A, Criado M. Microstructure development of alkali activated fly ash cement: a descriptive model. Cement Concrete Research., 2005;35(6):1204-9.
11. P. Duxson, J.L. Provis, Designing precursors for geopolymer cements, J. Am. Ceram.Soc. 91 (12) (2008) 3864–3869.
12. L. Weng, K. Sagoe-Crentsil, Dissolution processes, hydrolysis and condensation reactions during geopolymer synthesis: Part I — low Si/Al ratio systems, J. Mater.Sci. 42 (2007) 2997–3006.
13. LuoXinXu Jinyu1 ,Li Weimin3, Response surface design of solid waste 1 based geopolymer, www.rsc.org/advances, DOI: 10.1039/C4RA05458J
14. Menezes, R.R., Malzac, Neto, H.G., Santana, L.N.L., Lira, H.L., Ferreira, H.S., and Neves,G.A., (2008).“Optimization of wastes content in ceramic tiles using statistical design of mixture experiments”.Journal of the European Ceramic Society, 28, 3027–3039.
15. Myers, R.H. and Montgomery, D.C, (2002). “Response surface methodology: Process and product optimization using designed experiments”.2nd edition.Wiley, New York.
16. VioletaNikolica*, MiroslavKomljenovica et al., The inflennce
17. structure of geopolymers, Construction and Building Materials, (94)2015, 361-370
18. M. Sahmaran, M. Lachemi, V.C. Li, Assessing mechanical properties and microstructure of fire damaged engineered cementitious composites, ACI Materials Journal, 107 (2010) 297-304.
19. Multiple Responses: The Desirability Approach. Available online: http://www.itl.nist.gov/div898/handbook/pri/section5/pri5322.htm (accessed on 5 May 2016).
20. Promentilla, M.A.B.; Nguyen, H.T.; Pham, T.K.; Hirofumi, H.; Bacani, F.T.; Gallardo, S.M.Optimizing ternary-blended geopolymers with multi-response surface analysis. Waste Biomass Valoriz.2016.
21. Criado, M., Fernandez-Jimenez, A., Palomo, A., Alkali activation of fly ash. Part III: Effect of curing conditions on reaction and its graphical descriptionFuel, 89, 2010, p. 3185.
22. Maria Izquierdo, Xavier Querol, Joseph Davidovits, Diano Antenucci, Henk Nugteren, Constantino Fernández-Pereira, Coal fly ash-slag-based geopolymers: Microstructure and metal leaching. Journal of Hazardous Materials 166 (1) 561-566, 2009.
23. D. Dimas, L. Giannopoulou, D.Panias, Polymerization in sodium silicate solutions: a fundamental process in geopolymerization technology, J Mater Sci, 44, 3719–30 (2009).
24. Guo X, Huisheng Shi H, Dick WA. Compressive strength and micro structural characteristics of class C Fly Ash Geo Polymer. Cement Concrete and Composites. 2010 Feb; 32(2):142–7.24P.
25. Kamhangrittirong, P. Suwanvitaya, W. Witayakul, P. Suwanvitaya, P. Chindaprasirt, "Factors Influence on Shrinkage of High Calcium Fly Ash Geopolymer Paste", Advanced Materials Research, Vols. 610-613, pp. 2275-2281, 2013..
26. Al Bakri, A.M.M., Kamarudin, H., Nizar, I.K., Sandu, A.V., Binhussain, M., Zarina, Y., Rafiza, A.R.,Characterization and Design of Alkali Activated Binder for Coating Application Rev. Chim. (Bucharest), 64, no. 4, 2013, p. 382.
27. Yahya, Z., Abdullah, M.M.A., Hussin, K., Ismail, K.N., Sandu, A.V., Vizureanu, P., AbdRazak, R., processing and Characterization of Fly Ash-Based Geopolymer Bricks Rev. Chim. (Bucharest), 64, no. 12, 2013, p. 1408.
28. Ion, M., Vasile, V., Dobrescu, C., Urbanism. Arhitectura. Constructii, 2, no. 4, 2011, p. 77.
29. Buruiana, D.L., Bordei, M., Sandu, A.V., Chirculescu, A.I., Sandu, I.G., Mat. Plast., 50, no. 2, 2013, p. 113

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