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RESEARCH ARTICLE

Parametric investigation on the novel and cost-effective nano fly ash impregnated geopolymer system for sustainable construction

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ABSTRACT The hazardous environmental effects of greenhouse gas emissions and climate change demand alternative sources for cementitious materials in the construction industry. The development of geopolymer structures provides a way of producing 100% cement-free construction. In this research work, a novel and simple way of deriving nano particles from waste fly ash particles is promoted. The effect of adding the synthesized nano fly ash particles as a filler medium in geopolymer mortars was investigated by considering strength and durability properties. Parameter optimization was done by using regression analysis on the geopolymer mortar and the impact of adding nano fly ash particles was studied by varying different percentages of addition ranging from 0 to 7.5% by weight of binder content. From the results, it was observed that 1% nano fly ash acted not only as a filler but also as nano-sized precursors of the polymerization process, resulting in denser geopolymer medium. This can explain the extraordinary gain in strength of 72.11 MPa as well as the denser core with negligible level of chloride ion penetration, making the material suitable for the development of structures susceptible to marine environment.

KEYWORDS geopolymer, nano fly ash, chloride ion penetration, durability, polymerization, fillers

1 Introduction

Geopolymer is the focus of the emerging trend of research in which the cement is completely replaced by using alumina silicate minerals such as fly ash, slag and metakaolin and activated with the help of alkaline solution containing hydroxides and silicates of sodium or potassium compounds. However, the major drawback in fly ash application is its slow rate of gaining strength. The addition of Ground Granulated Blast-furnace Slag (GGBS) can offer synergetic effects that reduce the time for completing the geopolymerisation process. The determination of optimum addition ratio is a key factor in the strength gaining mechanism, which also depends upon the type of raw material used, transportation and storage level changes in the material properties [1]. On the other hand, when considering the activators, sodium ions are smaller than potassium atoms and the sodium-based activators allow a faster rate of geopolymerisation due to the particle dynamic effect. Also, due to the formation of strong passivation layered protection of the sodium-based activators, the resultant geopolymer composites showed significant improvement in the durability properties such as water absorption, resistance to sulfate attack, acid attack, etc. In terms of thermal stability properties, the potassium activators possess more resistance against fire exposure than the sodium-based activators [2]. But there is still a scarcity of literature on the potassium-based geopolymers. Regarding resistance against chemical penetration, geopolymers are highly conductive in nature as they are manufactured in alkaline environments and exhibit porous micro-structure. To fill the micro-structural pores, and to enhance durability against chemical attack, nano materials can be introduced in the geopolymer system [3].

Uniform distribution of silica nano-particles controls the leaching of calcium ions and stimulates the formation of calcium silicate hydrate (CSH) gels. The resultant

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denser microstructure leads to the improved permeability effect. Also, by limiting the addition of nano silica to 2% by weight of binder content, upto 25% improvement in the compressive strength along with the enhancement in the workability properties can be achieved [4]. The combined bridging effect offered by 2% nano silica and 1% nano alumina forms a higher rate of formation of amorphous gels, reducing the porosity and leaching effects and so increasing the rate of geopolymerisation [5]. The refining of micro structural voids is achieved by the nano filling effect offered by the nano alumina particles. Also, the presence of nano alumina in the alkaline solution results in enhanced gel formation by stimulating zeolite nuclei and inducing silica-oxygen-alumina (Si-O-Al) bonds in the geopolymer system [6]. Due to this effective void filling mechanism and nucleation effect provided by the nano alumina, the developed geopolymer mortars possess improved resistance to bending and impact [7]. It was reported that the significant enhancement in the durability parameters such as chloride ion permeability can be achieved by using nano alumina at 20% by volume of solid precursor along with 1% polypropylene in the development of lightweight geopolymer construction [8]. Adding nano titanium dioxide within the range of 0.5% to 2% by weight, a powerful photo-catalytic action has been initiated in the geopolymerisation process due to hydrophilic self-cleaning properties. This self-disinfectant nano titanium dioxide reduces pollution and provides bacteria-free concrete structures [9]. The nano calcium carbonate particles provide enhanced nucleation sites for the effective seeding of CSH gel, by stimulating the rate of hydration [10]. With the addition of 2% by weight of nano calcium carbonate, it has been seen that 39% improvement in the mechanical strength could be achieved due to the development of a nano compacted denser matrix [11]. It has been suggested that thermal conductivity has been highly improved by adding 1% carbon nano tubes by weight of binder content, due to their unique energy absorption nature and high aspect ratio [12]. In most nano material impregnated geopolymer concrete, for reasons of economy, many of the research works have been carried out using sodium based alkaline solution. Although sodium-based alkaline solutions are cheaper, the potassium-based activators resulted in enhanced durability properties in conditions of thermal exposure. As the molecular weight and melting point of the K^+ ions are higher than those of Na^+, the potassium-based alkaline activators are more durable in thermal exposure conditions [2,3].

To fill the research gaps on potassium-based activators and to establish economically viable nano-fillers for geopolymer construction, a novel, simple and cost-effective approach of deriving new nano-fillers from the fly ash wastes was developed. The efficacy of the developed nano-fly ash particles on the strength and durability properties of geopolymer mortar was studied experimentally. For this purpose, initially, the governing parameters such as binder composition, molarity of hydroxide solution and silicate-to-hydroxide ratio were optimized based on regression analysis in terms of compressive strength. Fly ash and GGBS were employed as binders, and the potassium-based alkaline solution was used as the activating solution, due to the lack of research work on thermally stable potassium-based alkaline solution in the context of the vast quantity of fly ash that is available. The effect of adding nano fly ash particles to property-optimized geopolymer mortar was studied experimentally by varying the percentage of addition from 0 to 7.5% by weight of binder content. From the compressive strength results, the percentage of added nano fly ash materials was optimized by using regression analysis. From the results, a novel geopolymer with optimum percentage of nano fly ash impregnation was developed and the strength and durability characteristics were studied by conducting compressive strength test, split tensile strength test, rapid chloride penetration test and chloride immersion tests, conforming to the ASTM standards. The interpretation of experimental results was done with the help of Scanning Electron Microscopic (SEM) analysis. To obtain the relationship between the proportional content of porous micro-structure and the compressive strength after chloride immersion, correlation analysis was done statistically. The durability properties of the property-optimized nano fly ash impregnated geopolymer mortar were compared with those of conventional geopolymer and cement mortar, to establish an alternative environmental-friendly binder system for structural application.

2 Materials and methods

Class F fly ash procured from Tuticorin Thermal Power Station, and GGBS purchased from Astra Chemicals, Chennai, were used as binders. Graded River sand conforming to Zone II of IS 383 was used as fine aggregate. Potassium hydroxide pellets and potassium silicate solution of density 1.33 g/cm^3 were employed as alkaline activators. Polycarboxylic ether was used as super plasticizer. To prepare a control specimen, Ordinary Portland Cement (OPC 53) was used as binder.

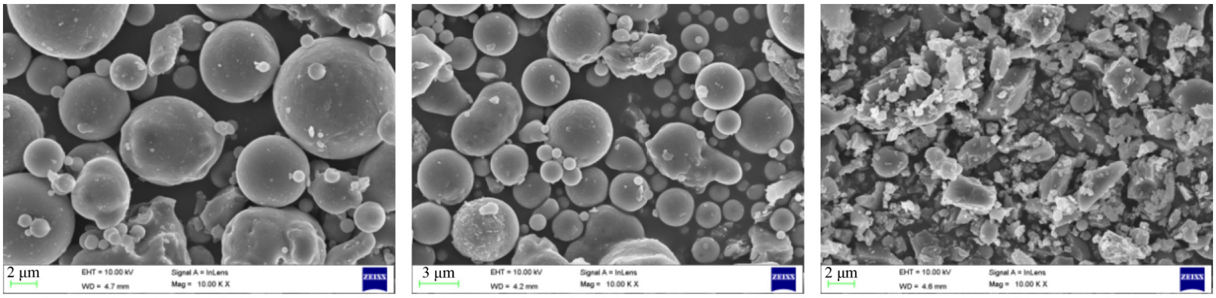
2.1 Deriving novel type nano-fillers from the fly ash wastes

The fly ash collected from different resources generally contains unburned carbon and ammonia content due to the action of electrostatic precipitators in the thermal power plants. These detrimental carbon impurities (loss-on-ignition content (LOI)) were removed from the fly ash by applying the temperature of 700 °C for 2 h [13]. The fly ash was allowed to cool after that thermal treatment for 24 h. Initially, the particle size of the fly ash particle was in the range between 110 to 120 microns. To reduce the particle size to nano level, first the fly ash particles were ground by using dry mixer grinder. Then the grinded fly ash particles were manually sieved using a 45 micron IS sieve. The fly ash particles passing through the IS 45 microns sieve had the particle size ranged from 38 to 45 microns, confirmed by the SEM analysis as shown in Fig. 1. Due to the thermal and physical pre-treatment process, the LOI content had been completely removed and the average particle size had been reduced to 40 microns.

The particles were further ground in the Planetary Mono Mill using 50 tungsten carbine balls, maintaining the powder to ball ratio as 1: 20. The speed of the ball mill was kept at 300 r/min and the grinding process was continued using toluene as a coolant for 8 h with a 7-min interval for each 15 min of milling. The ground mixture of fly ash and toluene was then taken from the ball mill and spread over a tray. In a few minutes the toluene solution used as the coolant for the wet grinding process was evaporated from the ground fly ash particles. Also, from the SEM analysis, it was confirmed that the ground particles had the average particle size of 76 nm, which is designated as nano fly ash. The mineral characterization of the fly ash at the three mentioned states, namely, initial stage, after pre-treatment, and after ball milling and GGBS, was done by using Energy Dispersive Xray Spectroscopy (EDAX) analysis. Also, by using the Bruker software in the EDAX analysis, the elemental compositions of the materials were directly converted into oxide composition as given in Table 1. The synthesized novel fly ash particles were used as fillers in the geopolymer matrix, in order to improve the strength and durability characteristics.

2.2 Mixoptimization and casting

Based on trial and error method, the mix proportions of geopolymer mortar was finalized as given in Table 2. In the finalized mix, the effect of varying four different parameters, namely binder composition (fly ash: GGBS), molarity of potassium hydroxide solution, silicate to hydroxide ratio and percentage of adding nano fly ash particles, were studied in four different stages as shown in Fig. 2. Initially, to optimize the binder composition, the other parameters such as molarity, Silicate to Hydroxide ratio (*S*/*H* ratio) and percentage of nano fly ash were kept constant at 12 M, 1.5, and 0%, respectively. The percentage of adding fly ash and GGBS was then varied from 0% to 100% by weight. After finalizing the binder composition based on the compressive strength, the



(a) (b) (c)

Fig. 1 Comparison of morphological structures of fly ash at: (a) initial stage; (b) after pre-treatment; (c) after ball milling.

Table 1 Comparison of element oxide composition

S.No	Material	Oxide composition (%)										
		Al_2O_3	SiO_2	CaO	FeO	K_2O	TiO_2	Cu	MgO	SO_3	Na_2O	LOI
1	raw fly ash	30.90	55.53	2.76	5.57	1.73	3.62	–	–	–	–	5
2	fly ash after pre-treatment	30.97	58.50	1.11	5.46	1.67	1.46	0.84	–	–	–	0
3	nano fly ash	28.40	63.24	0.96	5.28	1.07	1.05	–	–	–	–	0
4	GGBS	17.26	28.04	46.94	0.38	0.12	0.49	–	6.24	0.53	–	0

Table 2 Mix design achieved after trial and error process for the potassium based geopolymer mortar

S.No	Silicate to hydroxide ratio	Binder content (kg/m^3)	Fine aggregate (kg/m^3)	Potassium hydroxide (kg/m^3)	Potassium silicate (kg/m^3)	Super plasticizer (% by volume of binder)
1	1.5	857.14	1200	137.14	205.710	2%
2	2.5	824.00	1153	94.29	235.725	–

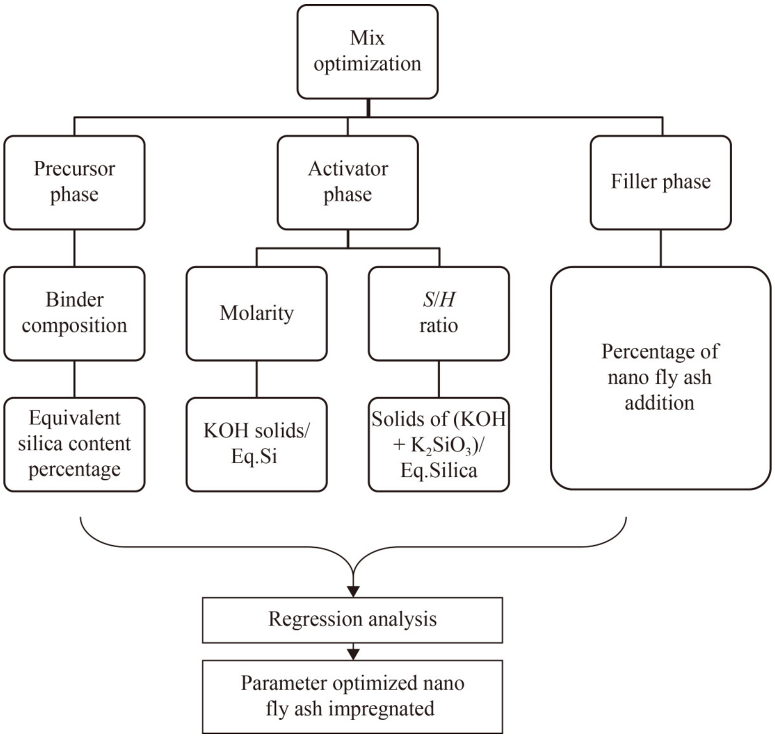


Fig. 2 Process of mix optimization.

variation in the molarity of potassium hydroxide solution and *S*/*H* ratio on the geopolymer mortar were studied.

An alkaline solution was prepared 24 h prior to the casting process. Also, the mixing of potassium hydroxide and silicate solution was done 30 min prior to the casting process. To achieve workability in the mixture, superplasticizer is recommended to be added from 0.5% to 2% volume of binder content [14,15]. While mixing, to achieve the desirable workability, the super plasticizer was added to the mix by 2% volume of the binder content based on the preliminary investigation conducted by the authors [16].

Cube specimens of size 70.6 mm × 70.6 mm × 70.6 mm were cast for each combination in order to study the influence of each parameter on the compressive strength. For the optimized parametric composition, a cylindrical specimen of diameter 100 mm and height 200 mm and cylindrical disc specimen of 50 mm thickness and 100 mm diameter were cast to study the split tensile strength and chloride ion permeability properties. After 24 h, the specimens were de-molded. The control cement mortars were cured under water curing for 28 d and geopolymer mortars was subjected to oven curing at the temperature 100 °C for 24 h.

2.3 Compressive strength test

After curing, 4 d rest period was given to each specimen to ensure the completion of hydration and polymerization processes. The compressive strength of mortars was found out by conducting compressive strength test as per the standards of ASTM C 109 [17]. The loading rate was increased at the rate of 2.9 kg·f/s. The load, at which the failure of the cube specimen took place, was considered as compressive strength of the specimen as given in Table 3. Based on the experimental trails, the governing mix parameters such as binder composition, molarity, *S*/*H* ratio, and percentage of nano fly ash were optimized using regression analysis. The micro structural changes of the failure specimen were studied using SEM analysis.

2.4 Split tensile strength

On the strength optimized geopolymer mortar, a split tensile strength test was carried out by confirming the standards of ASTM C 102. The cylindrical specimens of optimized geopolymer mortar and control cement mortar were placed horizontally in the compression testing machine. The loading was applied until the failure of the specimens as in the case of cube compression test.

2.5 Water absorption test

The presence of pores in the micro structure of the mortars was quantitatively assessed by conducting water absorption test conforming to the standards of ASTMC 1585. For this purpose, the mortars were burned initially at the temperature of 100 °C for 24 h. The mortars were allowed to cool at room temperature for another 24 h and then immersed in water for 60 d. The change in weight of mortars was continuously monitored at intervals of 15 d. The weight of the mortars before and after immersion

Table 3 Results of compressive strength test for various parameter

Specimen No.	Variable	Parametric variation	Maximum load (kN)	Compressive strength (MPa)
1	binder ratio (Fly ash/GGBS)	100/0	141.8	28.5
		60/40	207.2	41.6
		50/50	195.3	41.1
		40/60	196.0	39.4
		30/70	204.6	39.2
		0/100	147.0	29.7
		cement mortar	262.4	54.6
2	molarity of alkaline solution (for 60/40 binder mix)	10 M	138.7	27.8
		12 M	204.6	41.1
		14 M	383.4	64.4
3	*S*/*H* ratio (for 60/40 binder mix)	1.5	204.6	41.1
		2.5	261.4	52.4

was observed and the percentage of water absorption was calculated by using the Eq. (1):

$$\text{Percentage of water absorption} = \frac{W_1 - W_2}{W_2} \times 100\%, \quad (1)$$

where W_1 is the initial weight of the mortar before immersion and W_2 is the weight of mortars after immersing for the required period of time. The percentage of water absorption represents the degree of pores susceptible to external diffusion such as by water, chloride etc.

2.6 Rapid chloride penetration test

The durability properties of strength-optimized potassium-activated geopolymer mortars were tested by conducting Rapid Chloride Permeability (RCPT) test as per the standards of ASTM C1202 [18] as shown in Fig. 3. The cylindrical disc specimens were placed in between the 3% sodium chloride and 0.3 molar sodium hydroxide solutions for 6 h. The circumferential coating was applied on the specimen with the help of silicone gel in order to prevent the chloride ion run off. The permeability of chloride ions through the specimen was monitored with the help of data analog system. The net chloride ions passed from sodium chloride solution through the specimen at the end of 6 h was taken as RCPT value.

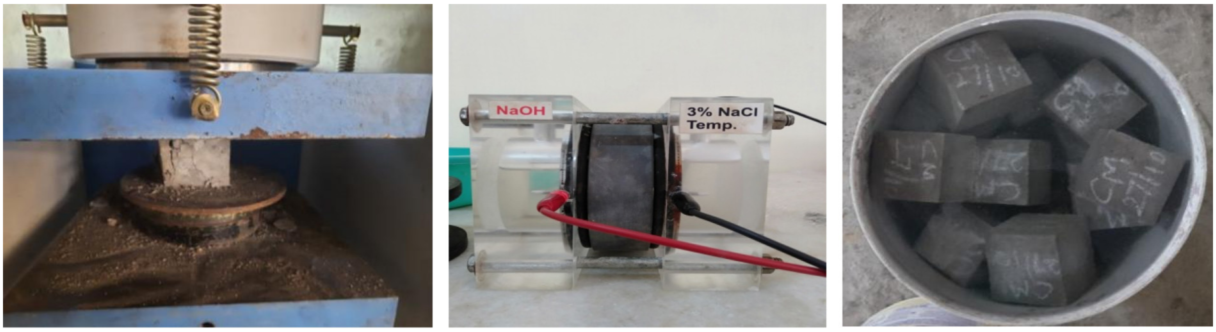
2.7 Immersion technique

To assess the real time application, the strength-optimized geopolymer mortar cubes were immersed in 3.5% sodium chloride solution for 60 d. The specimens were then taken out from the sodium chloride solution, cleaned and allowed to dry for 24 h in atmospheric conditions. The specimen was weighed before and after immersing in the sodium chloride solution. The loss in weight was calculated as a percentage and the strength retained after immersion was determined by conducting compressive strength tests.

3 Results and discussion

3.1 Parametric optimization

The optimum values of governing parameters such as binder composition, molarity of potassium hydroxide, *S*/*H* ratio and percentage addition of nano fly ash particles were identified by using compressive strength results.



(a) (b) (c)

Fig. 3 Testing of mortars: (a) compression test; (b) rapid chloride penetration test; (c) chloride immersion test.

Further, the durability studies were carried out on the parameter optimized geopolymer mortar and compared with the results for the cement mortar specimen.

3.1.1 Binder composition

While varying the composition of fly ash and GGBS in the binder system of geopolymer mortar, it was observed that increase in the addition of GGBS content upto 40% by weight, increased the compressive strength of geopolymer mortar by 31% compared to the result for the geopolymer mortar without GGBS. The calcium oxides present in the GGBS compound along with the silica enriched fly ash compound dissolved in the activators and resulted in the formation of more calcium aluminum silicate hydrate (CASH), CSH, and potassium aluminum silicate hydrate (KASH) gels, as observed from the SEM analysis.

Beyond 40% by weight of GGBS addition, the compressive strength of the geopolymer mortars were observed to decrease. At these increased percentage of GGBS addition, the presence of silica oxides was insufficient to form the CASH and CSH gels [19]. The excess unreacted calcium content present in the GGBS (Table 1) of geopolymer mortar contributed to the reduced compressive strength. By inferring from these results, the optimum binder proportion for achieving the maximum compressive strength was taken as 60% fly ash with 40% GGBS. This optimum binder combination will vary based on the Ca, Si and Al compounds present in the fly ash and GGBS system. To optimize the binder composition of the geopolymer mortars, regression analysis was carried out using the SPSS tool. In the statistical analysis, the oxide combinations of the binder system were taken as variables. The consequent changes in the oxide content of each mix combinations were considered in the analysis. At the end of regression analysis, a statistical equation was obtained to optimize the binder content. To validate the equation, the authors conducted further experimental study based on the results obtained from the optimization process. The extensive experimental studies confirmed the accuracy of the formulated regression equation [16]. Also, the results from statistical analysis were compared with the experimental values. Based on the binder composition (fly ash: GGBS), the total oxide compositions of the major constituents such as silica, alumina and calcium oxides were calculated. The ratio of the alumina to silica was taken as r_1 and the ratio of the calcium oxide to silica was taken as r_2. From this equivalent total silica content were calculated using the multipliers r_1 and r_2. The regression analysis was carried out between the equivalent silica and the corresponding compressive strength. The optimization of compressive strength for the variation in the equivalent oxide composition was done for any binder composition using Eqs. (2) and (3). These equations confirmed the relationship between the various oxide compositions of the binder content as suggested by Reddy et al. [20].

$$c = -3.97 \times 10^{-3} - 0.45 \times \mathrm{Si.Eq} + 9.32 \times \mathrm{Si.Eq}^2, \quad (2)$$

$$\mathrm{Si.Eq} = \mathrm{SiO_2} \times (1 + r_1 + r_2), \quad (3)$$

In Eqs. (2) and (3), c denotes the compressive strength, Si.Eq is the equivalent silica content; SiO_2 is the total silica content present in the binder in percentage. The optimization equation followed the quadratic path with the root mean square value of 0.854 as shown in Fig. 4.

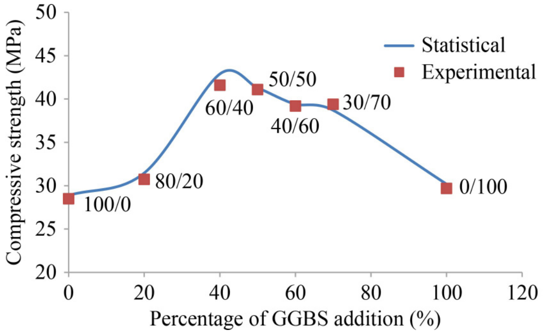


Fig. 4 Comparison of statistical and experimental compressive strength.

It was observed that the regression analysis results of binder composition were well matched with the experimental results. The statistical results were suitable for optimization of the binder composition of any type of binder. Eqation (2) is constructed for the geopolymer mortar with binder to aggregate ratio of 1:1, 12 mol/L molarity of potassium hydroxide solution, silicate to hydroxide ratio in the alkaline media of 1.5 and curing temperature of 100 °C for 24 h.

3.1.2 Molarity of alkaline solution

From comparing the compressive strength results of potassium activated geopolymer mortars with varying molarities in the alkaline solution, it is understood that compressive strength of mortars increased with the increase in the concentration of potassium hydroxide solution. When using 10 mol/L potassium hydroxide solution the geopolymer mortar develops only 27.8 MPa strength, which is 48% lower than that of the optimized mortar having 12 mol/L concentration. In contrast, the use of 14 mol/L activators enhanced the compressive strength to 64.4 MPa, which is 35% higher than that of 12 mol/L mortars having the same precursor phase. The highly viscous potassium hydroxide solution at the increasing molarity of alkaline solution attributed to the enhanced strength characteristics. During the increase in concentration of potassium hydroxide solution, the dissolution process of the silica and alumina has taken place at a higher rate and acts as the foundation for the development of geopolymer systems. At the same time, the excess increase in the molarity led to the dispersion of free hydroxide compounds, which contributed to the precipitation of alumina silicate gels and resulted in the reduction in the strength [21].

To optimize the molarity of potassium hydroxide solution, the solids of potassium hydroxide to equivalent silica content present in the binder were taken as the major variable. The regression analysis was done using the ratio of total solids of potassium hydroxide present (Eqs. (4) and (5)) in the alkaline solution to the equivalent silica as well as the quadratic optimization equation as given in Eq. (6). This acted as a curve estimation technique, producing results as shown in Fig. 5.

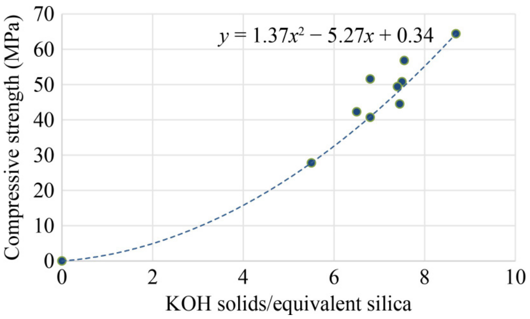


Fig. 5 Optimization of molar concentration.

$$r_3 = \text{KOH solids/Si.Eq}, \tag{4}$$

r_3 is the ratio of potassium hydroxide solids to equivalent silica content present in the binder system. Total solids in the potassium hydroxide solution:

$$\text{KOH solids} = \text{molecular weight} \times \text{molarity}. \tag{5}$$

$$c = 0.34 - 5.17 \times r_3 + 1.37 \times r_3^2, \tag{6}$$

The quadratic regression equation has the root mean square value of 0.859. This optimized equation is well suitable to calculate the compressive strength of any geopolymer mortar with varying binder composition and different molarity. The optimization equation is derived for the 1:1 mortar with *S*/*H* ratio of 1.5 and at the curing temperature of 100 °C for 24 h.

3.1.3 Silicate to hydroxide ratio

Similarly, the improvement in the *S*/*H* ratio by 2.5 results in the enhanced compressive strength of 52.4 MPa which was 20.6% higher than the geopolymer mortar having the *S*/*H* ratio of 1.5. This confirmed the results obtained by Hosan et al. [10] while conducting comparative study on the compressive strength behavior of potassium based geopolymer, varying the *S*/*H* ratio from 1.5 to 3 in which it was concluded that the improvement in the *S*/*H* ratio highly influenced the enhancement of its mechanical strength up to 2.5. Also, the improved rate of *S*/*H* ratio by 2.5 results in the economical mode of developing geopolymer.

For the regression analysis, the total solids in the alkaline medium to equivalent silica in the binder ratio was kept as variable. The optimization of the *S*/*H* ratio was done by using the relation between the solid content dissolved in the alkaline medium and the equivalent silicate present in the binder content as shown in Fig. 6.

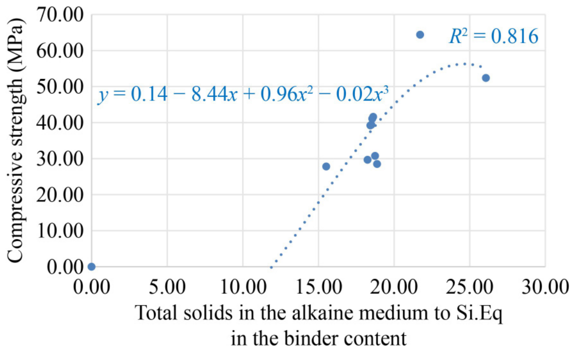


Fig. 6 Optimization of *S*/*H* ratio.

$$\begin{aligned}&\text{Total dissolved solids in the activators}\\&= \text{KOH soilds} + K_2SiO_3 \text{ soilds},\end{aligned} \tag{7}$$

$$K_2SiO_3 \text{ solids} = (S/H) \times \text{KOH solids}, \tag{8}$$

$$\text{Multiplier } r_4 = (\text{KOH} + K_2SiO_3) \text{ solids/Si.Eq}, \tag{9}$$

$$c = 0.14 - 8.44 \times r_4 + 0.96 \times r_4^2 - 0.02 \times r_4^3. \tag{10}$$

The optimized equation follows the cubical path with the root mean square value of 0.819. This optimized equation is obtained for the 1:1 geopolymer mortar cured at the temperature of 100 °C for 24 h. Equation (10), considers the combination of binder content, molarity of alkaline solution and silicate to hydroxide ratio at the same time.

3.1.4 Percentage of nano-fillers

After optimizing the binder and activator phases of the geopolymer mortar, the filler phase was optimized by using the newly developed nano fly ash particles. The nano fly ash particles derived from the pre-treatment and ball milling procedure as explained in the Subsection 2.1, were added on the optimized geopolymer mortar in 0%, 2.5%, 5%, and 7.5% by weight of binder content. From the experimental results, it was observed that, the geopolymer mortar with optimized binder composition, molarity and *S*/*H* ratio exhibited the compressive strength of 64.4 MPa. The compressive strength of the optimized geopolymer mortar changed to 67.3, 52.7, and 42.11 MPa while impregnating the nano fly ash filler in the percentage of 2.5%, 5%, and 7.5% by weight of binder content, respectively. To obtain the optimum percentage of nano fly ash content, the regression analysis was carried out using the percentage of nano fly ash as the input variable. The results suggested that the maximum compressive strength of 73.2 MPa was obtained at the optimum percentage of 1% by weight of nano fly ash as given in Eq. (11).

Predicted compressive strength, *C*

$$C = 65.476 + 0.788 \times r_{\mathrm{n}} - 0.54 \times r_{\mathrm{n}}^2, \tag{11}$$

In Eq. (11), the variable r_{n} represents the percentage of added nano fly ash, ranging from 0% to 10%. To validate the statistical results, the geopolymer mortar was cast by impregnating the optimum percentage of 1% by weight of nano fly ash. It was observed that the addition of 1% nano fly ash to the geopolymer mortar exhibited the compressive strength of 72.11 MPa, thus showing a good fit with the statistically optimized Eq. (11), as shown in Fig. 7.

It was observed that while increasing the percentage of nano fly ash upto 1% by weight of binder content the compressive strength of the geopolymer specimen was increased to the maximum of 72.11 MPa, which is 24% and 7.74% higher than values for the cement mortar and geopolymer mortar with 0% nano fly ash, respectively. The efficient pore filling properties of nano fly ash particles on the geopolymer mortar exhibited improved compressive strength. When increasing the percentage of nano fly ash beyond 2.5% by weight of binder content, the compressive strength of the specimen decreased drastically due to the agglomeration of nano particles as shown in Fig. 8(c). It was observed that due to the agglomeration of nano fly ash particles, the voids in the KASH gels were not efficiently filled and the agglomerated unreacted nano particles caused inefficiency in the pore filling mechanism and created weaker zones of wider pores around the KASH gels [22,23]. This attributes to the significant reduction in the compressive strength at the increased percentage of nano fly ash addition. From the results, it was concluded that the maximum strength of 72.11 MPa was obtained with the geopolymer specimen if the nano fly ash addition was limited to the optimum percentage of 1% by weight of binder content.

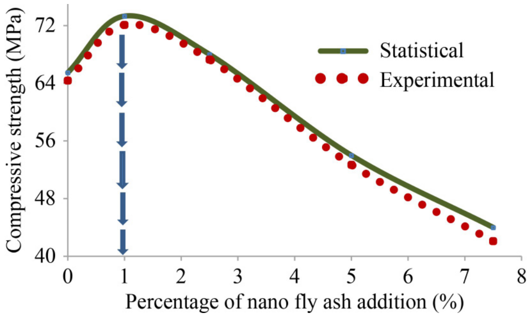
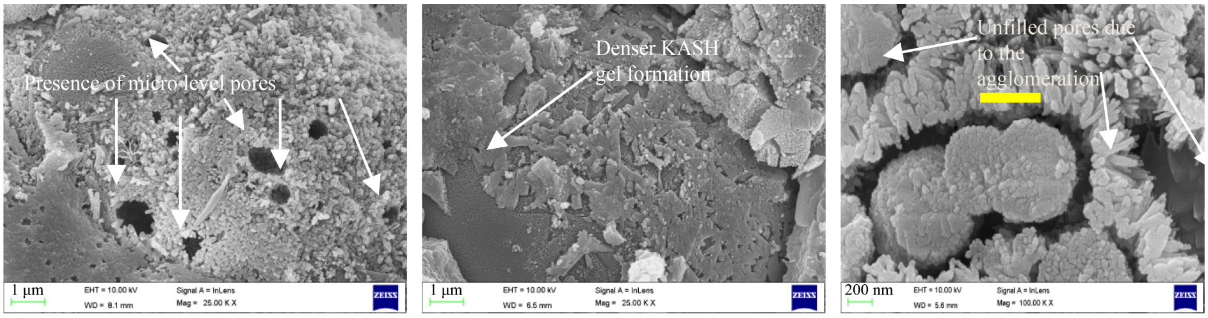


Fig. 7 Change in the compressive strength for the various percentage addition of nano fly ash.

3.2 Split tensile strength

From the parametric studies, the optimum binder composition, molarity and *S*/*H* ratio of the potassium based geopolymer mortars were found to be 60% fly ash with 40% GGBS, 12 M, and 2.5, respectively. For the optimized mix of nano fly ash impregnated geopolymer mortar, the split tensile strength test was carried out and the result was compared with the conventional cement concrete specimen. It was found that the cement mortar exhibited the split tensile strength of 5.6 MPa. The optimized geopolymer mixes with 0% and 1% nano fly ash impregnation exhibited split tensile strengths of 6.32 and 7.2 MPa respectively.

The extreme brittleness of the cement mortar attributed to the decreased tensile strength. From the morphological characteristic analysis done by Liu et al. [24], it was



(a) (b) (c)

Fig. 8 FESEM results of parameter optimized geopolymer mortar with: (a) 0% nano fly ash; (b) 1% nano fly ash; (c) 2.5% nano fly ash.

concluded that the stability of the geopolymer mortar against the applied stress purely depends upon the rate of formation of KASH gels. The better interfacial bonding offered by the denser KASH gel formation (as confirmed by the X-ray Diffraction (XRD) results), contributed to the improved tensile strength, as shown in the FESEM analysis. The denser the formation of KASH gels, the lower the proportion by volume of voids in the geopolymer mortar. This resulted in improvement in the integrity of the tensile stress traveling path [25] and attributed to the 12.23% improved tensile strength in the 1% nano fly ash impregnated geopolymer mortar compared with that for the counterpart geopolymer with 0% nano fly ash.

3.3 Water absorption

When comparing the rate of water absorption by traditional cement mortar with that by geopolymer mortar, with and without fly ash, it was observed that the rate of water absorption increased gradually with increase in immersion time and with availability of pores in the microstructure.

Figure 9 shows that the geopolymer mortar without nano fly ash exhibited the highest percentage of water absorption at every stage. The porous nature of the formulated KASH gels, contributes to the 48%–83% rapid increase in the water absorption of geopolymer mortar above that of the cement mortar specimens. When adding the nano fly ash to the geopolymer mortar, the surface pores were efficiently filled by formulating the additional KASH gels as shown in Fig 10. The resultant densely packed geopolymer mortar offers 42% to 47% improved resistance against external ionic permeation compared to the conventional cement mortar.

3.4 Resistance against chloride permeation

From the chloride ion permeability test, it was observed that the cement mortar exhibited RCPT value of 2587 C which is a moderate level of permeability as given by the ASTM C 1202 [18]. But the optimized geopolymer mortar with 1% nano fly ash exhibited only 70 C, which is classified as a ‘negligible’ level permeability. The RCPT value of the geopolymer mortar with 0% nano fly ash was observed to be 1856 C which is 28% lesser than cement mortar. The pre-treatment applied to the fly ash binder system effectively reduced the proportion by volume of pores present in the micro structure and resulted in the lower value of RCPT in the geopolymer mortars than in the cement mortar. Further, addition of 1% nano fly ash efficiently filled the pores and the micro structures of the geopolymer mortar and showed the denser formation of KASH and CASH gels as mentioned in the Fig. 8. The voids present in the micro structure were filled with the help of closely space poly sialate-siloxo (-Si-O-Al-O-Si-O-Si-O-) polymers. This contributed to the very low percentage of chloride ion permeability. Also, this enhanced micro structure resulted in the residual compressive strength of 62.16 MPa (which is only 13.7% reduction compared with the original strength) after 60 d of immersing in 3.5% sodium chloride solution.

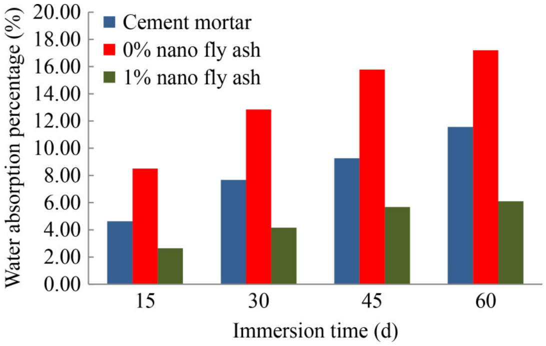


Fig. 9 Comparison of water absorption percentage of mortars.

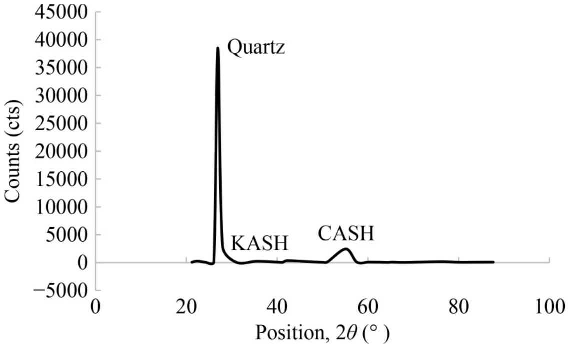


Fig. 10 XRD results of nano fly ash impregnated geopolymer mortar.

When the cement mortar was subjected to chloride exposure condition, the chloride ions penetrated through the surface pores and reacted with the alumina compounds of the cement and initiated the development of mono chloro-aluminate which is known as Friedel salt. The generated salt was absorbed on the surface of the hydrated gels and deteriorated the cement mortar system [26]. Due to this chloride attack, the cement mortar retained with 93%, 88.8%, 74%, and 66.3% of the original compressive strength at the end of 15, 30, 45, and 60 d of sodium chloride immersion, respectively. In the case of geopolymer mortars impregnated with nano fly ash, the void filling effect of nano fly ash particles attributed to the enhanced formation of KASH and CASH gels in micro level pores and resulted in the denser geopolymer mortar. Also, the enhanced reactivity of the fly ash resulted in the formation of quartz compounds which enhanced the stability of the mortar against chemical diffusion as shown in XRD test results. The quartz (near the peak observed at the angle of 26.04°) is highly resistant to chloride solution [27]. This stability of the formed quartz compounds enhanced the durability of the geopolymer mortar against chloride diffusion. It is significant to note that the reactivity of quartz compound in the precursor phase was stimulated by the employed pre-treatment methods and activated by the potassium silicate and hydroxide solution. So, the resultant quartz compounds possessed high reactive potential which was confirmed by the amorphous pattern of the XRD curve. Also, there are no significant peaks observed near the angle (2θ) between 32° and 44° which showcased the chloride-resistance behavior of geopolymer mortars. The strong covalent bonds that existed between the silica and oxygen atoms induced the sustainability of the mortars against chloride diffusion. The produced quartz content involved in the alkaline medium enhanced the polymerization, resulting in the formation of strong KASH and CASH gels [28] as indicated in Fig. 10. This contributed to the formation of a strong and denser micro structure with enhanced resistance against chloride ion penetration.

This increased resistance against penetration by chloride ions resulted in retention of 96.24%, 92.6%, 89.6%, and 86.2% of the original compressive strength after immersion in sodium chloride solution for 15, 30, 45, and 60 d, (Fig. 11) respectively. Thus, the developed geopolymer mortar system impregnated with nano fly ash offered higher resistance to chloride permeability than was the case for the cement mortar, and can lead to the development of geopolymer construction in the marine environment with the help of newly developed nano fly ash materials.

3.5 Correlation analysis

The level of refining the porous micro structure in the geopolymer medium decides the degree of chemical infiltration and the corresponding sustainability of the geopolymer system in aggressive environments. Hence, by keeping the percentage of water absorption as the influencing factor, the correlation with the residual compressive strength of the mortars after immersing in sodium chloride solution was obtained from the statistical tool, SPSS. The bivariate correlation analysis was done using the Pearson correlation method.

From the results (Table 4), a 2 × 2 correlation matrix was formulated between the variables and the correlation coefficient was found to be 0.732. Generally, the Pearson's correlation coefficient value ranged from + 1 to −1, in which + 1 indicates the perfect positive correlation and the −1 represents the negative correlation. If the correlation coefficient is 0, then there is no linear correlation between the chosen variables. In this case, the obtained correlation coefficient 0.732 indicates the most predominant factor which decides the residual strength of mortar was the percentage of water absorption i.e., the level of pores present in the mortar to allow permeation. The value of significance obtained from the correlation analysis is 0.007, which is greater than 0. This means the relationship between the two variables are highly significant and not with random sampling error. To obtain the quantitative relation between the percentage of pores prone to water absorption and the strength retained after chloride immersion, regression analysis was carried out as shown in the Eq. (12):

$$\begin{aligned}&\text{Retained percentage of strength}\\&= 101.445 - 0.924 \times p - 0.228 \times t,\end{aligned} \tag{12}$$

where p is the percentage of water absorption pores and t is the immersion time period.

It was observed that the percentage of retained strength

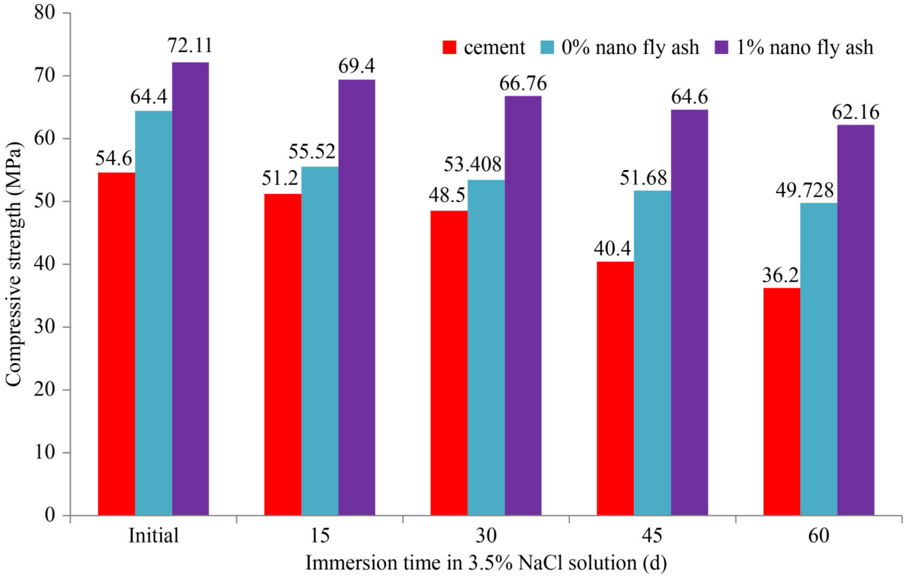


Fig. 11 Comparison of results of optimized mortar with cement mortar.

results obtained from Eq. (12) matched with the experimental results as given in Fig. 12. It was also observed that the rate of reduction in the strength highly depends on the porous nature of the mortar specimen and the immersion time period. The good distribution of nano fly ash on the geopolymer mortar effectively filled these microstructural pores and the resultant closely packed mortar offered high resistance against chloride ion permeation. This contributed to the highest percentage of strength retaining ability in the geopolymer mortar impregnated with 1% nano fly ash, compared with values for the control cement and geopolymer mortars.

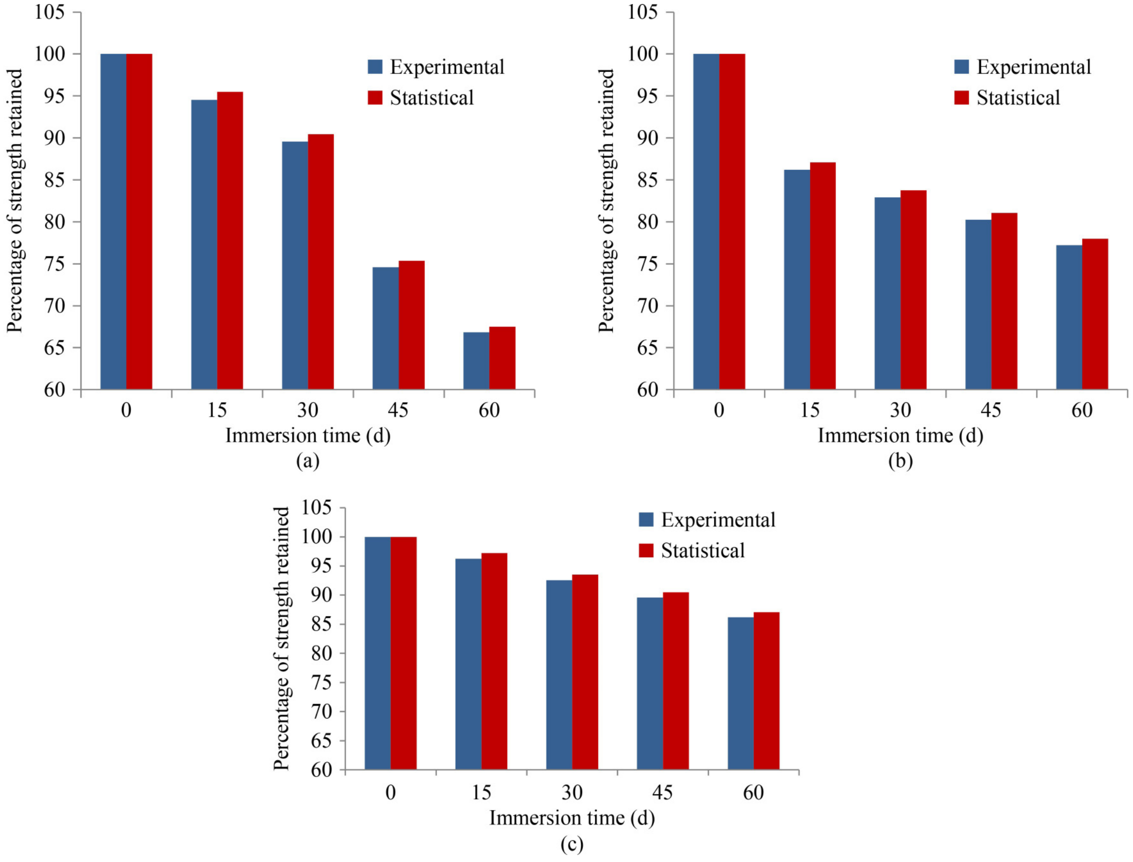
3.6 Cost effectiveness

To evaluate the superior properties of the developed nano fly ash particles on the geopolymer mortar, a comparative literature survey was carried out on the existing

Table 4 Result of Pearson Correlation analysis

Result of Pearson Correlation analysis	Water absorption (%)	Percentage loss in strength after immersing in sodium chloride solution
Water absorption %		
Pearson Correlation	1	0.732^{**}
Sig. (2-tailed)	–	0.007
N	12	12
Percentage loss in strength after immersing in sodium chloride solution		
Pearson Correlation	0.732^{**}	1
Sig. (2-tailed)	0.007	–
N	12	12

Notes: Correlation is significant at the 0.01 level (2-tailed).



(a)

(b)

(c)

Fig. 12 Comparison of percertage loss in strength obtained from experimental and statistical results: (a) cement mortar with 4.53%−11.56% pores; (b) geopolymer mortar 0% nano fly ash 8.5%−7.21% pores; (c) geopolymer mortar 1% nano fly ash 2.64%−6.1% pores.

geopolymer mortars with other nano particles as given in Table 5. It was observed that when compared to geopolymer mortars impregnated with other nano materials such as nano silica, titanium dioxide, silver, Multi Walled Carbon Nano Tube (MWCNT) etc., the developed nano fly ash particles exhibited maximum strength and enhanced resistance against chloride ion penetration.

Also, while considering economy, the cost of other nano materials ranged from Rs.300 to 24900 /kg, which significantly increase the cost of construction. In case of developed nano fly ash particles as the raw material, derived from the industrial waste, no material cost (excluding transportation and pre-treatment) is required to be invested and leads to the development of economic, environmentally friendly and sustainable geopolymer structures. The only cost involved in the derivation of nano fly ash is the power consumption required to run the ball mill which has energy consumption of 1.1 kWh.

4 Conclusions

In this work, a novel, simple and cost-effective approach of deriving nano material from fly ash wastes was carried out, using the geopolymer system as filler material. Initially, the key factors which influence the properties of geopolymer mortar, such as binder composition, molarity of hydroxide solution and the silicate to hydroxide ratio, were studied experimentally and were optimized using regression analysis. With parameter optimized geopolymer mortar, the effect adding nano fly ash particles was studied by varying the percentage of addition from 0 to 7.5% by weight of binder content, in order to find the optimum percentage of nano fly ash. The efficiency of the synthesized nano fly ash particles on the strength and durability characteristics of geopolymer mortars were studied in detail by conducting compressive strength, split tensile strength, rapid chloride penetration and immersion technique, and compared with results for existing cement mortars. From the results, the following conclusions were made.

1) The addition of GGBS upto 40% by weight in the fly ash content improved the compressive strength of the geopolymer mortar due to the formation of CASH gels from the calcium rich GGBS. Beyond 40%, the compressive strength gradually reduced as excess calcium ions remained unreacted on the surface.

2) The ratio of alumina to silica (r_1) and calcium oxide to silica (r_2) are the essential parameters to be considered for the optimization of binder composition with respect to compressive strength. The optimized equation formed by considering the total oxide composition of binder content predicts the compressive strength of the geopolymer mortars with aquadratic path.

3) The increase in the molarity of the potassium hydroxide solution increased the compressive strength due to the improved density of functional hydroxide groups. This induced rapid dissolution of silica and alumina minerals and resulted in the highest compressive strength of 64.4 MPa with 14 mol/L geopolymer mortars.

4) The optimization of molar concentration of alkaline solution, by considering the ratio between total solid present in the alkaline solution and equivalent silica in the binder content, resulted in a quadratic regressive expression which showed similar results as that of the experimental work.

5) Increase in the S/H ratio upto 2.5 increased the compressive strength by 20% higher than that of the mortars with the S/H ratio of 1.5.

Table 5 Comparison of the developed nano fly ash with other nano particles in the geopolymer environment

Type of nano filler	Percentage of addition by weight of binder (%)	Compressive strength (MPa)	Split tensile strength (MPa)	RCPT value (C)	Changes measured after chloride immersion	Cost of nano filler	Ref.
Nano silica (4−16 nm)	6	42.84	4.02	1121	7.07% mass loss after 28 d	Rs.300 /kg	[29]
Multi walled carbon nano tubes (14−24 nm)	0.1	20.601	–	–	–	Rs.249 /g	[30]
Nano silica (80 nm)	5	65	–	–	–	Rs.300 /kg	[31]
Nano silica (12−22 nm)	3	69.7	–	–	–	Rs.300 /kg	[32]
Nano silica (12 nm)	6	44	5.2	1100	–	Rs.300 /kg	[33]
Nano silver + nano silica (20−50 nm)	6	42	4.2	1000	–	Rs.500 /kg + Rs.300 /kg	[34]
Nano silica (15 nm)	2	70	–	–	–	Rs.300 /kg	[35]
Nano titanium dioxide (30 nm)	5	53.59	6.8	1000	–	Rs.890 /kg	[36]
Nano silica (12 nm)	4	62	–	–	–	Rs.300 /kg	[3]
Nano fly ash (76 nm)	1	72.11	7.2	70	62.16 residual strength after 60 d	Rs.127.6 /kg	present work

6) The addition of nano fly ash in the range 1%−2.5% by weight of binder content efficiently filled the surface pores; the maximum compressive strength of 72.11 MPa was achieved when adding 1% by weight of binder content. Excess addition of nano fly ash resulted in the significant reduction in the compressive strength due to the agglomeration of nano particles.

7) The optimized geopolymer mortar with 1% nano fly ash addition, showed closely packed micro structure with more formations of KASH and CSH gels which contributed to the reduced RCPT value of 70 C, which lies in the category of negligible chloride ion penetration.

8) Also, the denser micro structure formulated with the help of 1% nano fly ash impregnation resulted in the higher sustainability of geopolymer mortars with 86% retained compressive strength after immersion in 3.5% sodium chloride solution for 60 d.

9) The results of correlation analysis also confirmed that the predominant influencing factor which affects the sustainability of mortar against chloride ion diffusion was its porous micro structure. The efficient pore filling ability of the nano fly ash contributes to the formation of densely packed micro structure and resulted in the 47% reduced pore concentration relative to the case for cement mortar.

10) While comparing the cost of other existing nano material impregnated geopolymer mortar, the use of nano fly ash results in the highly durable and sustainable geopolymer mortar in a cost-effective way.

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Competing interests The authors declare that they have no competing interests.

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