Study on Development of Geopolymer Binder from Terracotta Roof Tile Waste by Experimental and Statistical Method

S Usha, Deepa GNair, Subha Vishnudas

Research Scholar, Division of Civil Engineering, School of Engineering, CUSAT, Kochi, India
Faculty, Division of Civil Engineering, School of Engineering, CUSAT, Kochi, India

Abstract: Alkali activation of aluminosilicate materials produces geopolymers at ambient or slightly elevated temperatures by geopolymerization process. The reaction product is an amorphous aluminosilicate gel having a structure similar to that of zeolitic precursors. In this paper study on development of geopolymer binder from terracotta tile waste was carried out through experimental and statistical analysis. Compressive strength test was conducted with sixteen combinations of specimens by varying four identified parameters. A 2^4 full factorial design was adopted for the experimental study with each parameter having two levels. The significance of parameter effect on geopolymerization has been investigated using full factorial design. The influence of the parameters such as molarity of sodium hydroxide, alkali activator to binder ratio and elevated curing temperature on geopolymerization are found significant whereas influence of sodium silicate to sodium hydroxide solution ratio was insignificant at 5% level of significance. The interaction effect among the parameters are studied and found to be negligible.

Keywords: alkali activator, aluminosilicate, geopolymer, molarity, strength.

1. INTRODUCTION

Geopolymer binders can be used as an alternative to ordinary portland cement, which are amorphous to semi crystalline polymeric products. Raw materials of geopolymers are mainly silica and alumina rich natural materials / waste materials / by-products from industries. Utilization of waste materials in geopolymerization process lowers the energy requirement and minimizes CO_2 production, which enhances geopolymer as sustainable material. Alkali activation of aluminosilicate materials with alkaline silicate solution at room temperature or slightly higher temperatures forms the geopolymer.

The parameters influencing the geopolymerization of aluminosilicate materials as identified from the literature review are molarity of sodium hydroxide, sodium silicate to sodium hydroxide ratio, alkali activator to binder ratio and elevated temperature curing [1]. Palomo et al. [2] and many others confirmed that the concentration of the alkaline activator mainly affect the polymerization reaction [3], [4]. Sodium silicate addition to sodium hydroxide solution as an alkali activator enhances the reaction between the source material and the solution [5], [6]. High temperature curing has a positive effect on strength which increases the reaction at initial stage [7]. So far research on geopolymer was mainly concentrated on fly ash, a by-product from coal industry in which the best optimal physical and mechanical properties were reported with elevated curing temperature [7], [8], [9]. The optimized polymerization
parameters for different materials are observed as concentration of NaOH in the range of 7M to 12M, alkali to binder ratio in the range of 0.35 to 1 [10], [11] curing temperature in the range of 60°C to 75°C [2], [3], [11], [12] and sodium silicate to sodium hydroxide ratio as 2.50 [2], [3].

At ambient temperature, the geopolymerization of the raw fly ash is extremely slow [7], which was improved by mechanical activation or addition of ground granular blast furnace slag to fly ash [13], [14], [15], [16]. In recent years many investigations has been carried out to explore the possibility of utilizing locally available materials as raw material in the production of geopolymer cements [10], [17], [18]. Puertas et al. conducted experimental study and statistical analysis to investigate the effects of parameters on compressive strength [7].

The traditional Terra cotta tile industries of Kerala produced damaged / faulty tiles during the manufacture of terracotta roof tile. Old tiles from dismantled traditional houses were also added to the waste. This paper illustrates the influence of identified parameters in geopolymerization of terracotta roof tile waste (TRTW) through experimental and statistical analysis.

2.MATERIALS AND METHODS

2.1.Materials
Terracotta roof tile waste used for this study was collected from Kalady, Kerala. It was then crushed and powdered in ball mill to a particle size less than 75µm. Particle size distribution curve of the powder obtained by the hydrometer analysis is shown in Fig. 1. The image obtained from Scanning Electron Microscope(SEM) analysis is shown in Fig. 2. The chemical composition of the waste powder by X-Ray Fluorescence (XRF) analysis is tabulated in Table.1. The properties of the materials used for the experimental work is displayed in Table.2.

![Particle size distribution curve](image1.png)  
![SEM image of TRTW](image2.png)

Table.1.Mineralogical composition of TRTW

| Compound | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO | K₂O | TiO₂ | CaO | Na₂O | P₂O₅ | MnO |
|----------|------|-------|-------|-----|-----|------|-----|------|------|-----|
| % Weight | 54.79 | 30.66 | 9.54  | 0.82| 1.49| 1.24 | 0.56| 0.30 | 0.21 | 0.06|
Table 2. Properties of the materials

| Material          | Property     | Value |
|------------------|--------------|-------|
| TRTW             | Specific gravity | 2.8   |
| River Sand       | Specific gravity | 2.8   |
|                  | Fineness Modulus | 2.93  |
| Sodium Hydroxide pellet | Purity | 97%   |
| Sodium silicate solution | grade | Extra pure |
|                  | density      | 1.39g/cm³ |
|                  | pH           | 11.2  |

2.2 Experimental programme

Pilot study was conducted to investigate the influence of parameters such as molarity, alkali to binder (A/B) ratio, sodium silicate to sodium hydroxide solution (SS/SH) ratio, elevated curing temperature. Sixteen different combinations by varying the identified parameters with designations GP1 to GP16 were prepared and tested for compressive strength. The details of parameters involved in the experimental programme and the results are shown in Table 3.

Table 3. Details of parameters involved in the experimental programme and the results

| Mix ID | Molarity (M) | SS/SH ratio | A/B ratio | Temperature (°C) | 7th day compressive strength (N/mm²) |
|--------|--------------|-------------|-----------|------------------|--------------------------------------|
| GP1    | 10           | 2           | 0.6       | 55               | 5.2                                  |
| GP2    | 12           | 2           | 0.6       | 55               | 7.2                                  |
| GP3    | 10           | 2.5         | 0.6       | 55               | 6.0                                  |
| GP4    | 10           | 2           | 0.8       | 55               | 7.5                                  |
| GP5    | 10           | 2           | 0.6       | 65               | 5.4                                  |
| GP6    | 12           | 2.5         | 0.6       | 55               | 9.5                                  |
| GP7    | 10           | 2           | 0.8       | 65               | 14.2                                 |
| GP8    | 10           | 2.5         | 0.8       | 55               | 12.0                                 |
| GP9    | 12           | 2           | 0.6       | 65               | 13.5                                 |
| GP10   | 10           | 2.5         | 0.8       | 65               | 14.5                                 |
| GP11   | 12           | 2.5         | 0.8       | 55               | 18.6                                 |
| GP12   | 12           | 2           | 0.8       | 65               | 22.5                                 |
| GP13   | 12           | 2.5         | 0.6       | 65               | 18.2                                 |
| GP14   | 12           | 2           | 0.8       | 55               | 19.6                                 |
| GP15   | 10           | 2.5         | 0.6       | 65               | 7.5                                  |
| GP16   | **12**       | **2.5**     | **0.8**   | **65**           | **23.1**                             |
TRTW powder and river sand (1:3) were mixed in dry state and alkali activator was added in fixed proportion (activator to binder ratio 0.6 and 0.8). Thorough mixing was conducted to ensure complete reaction. Alkaline activator used for the sample was prepared one day prior to the casting of the specimen for proper compaction and moulding. The geopolymer mortar specimens (70.6mm x 70.6mm x 70.6 mm) were casted and kept at elevated temperatures 55°C or 65°C for 24 hours. The demoulded specimens were kept at room temperature for 6 days and then tested.

2.3 Results and discussion

The maximum compressive strength is observed with specimen GP16, in which the parameters involved are Molarity 12M, SS/SH ratio 2.5, A/B ratio 0.8 and elevated curing temperature at 65°C for 24 hours and remaining at room temperature. Fig.3 shows the SEM image of the sample GP16. On comparing Fig.2 and Fig.3, the geopolymer gel formation can be confirmed.

Fig.3 SEM image of geopolymer from TRTW

2.4 Statistical method

Analysis of variance (ANOVA) is a statistical technique used to investigate and model the relationship between a response variable and independent variables. Each independent variable consists of more than two levels. Effect sizes decide the significance of the reaction. Calculations in ANOVA determine the significance of each factor based on these effect calculations. To visualize effect size, main effect plots are used. In determining the main effects for each factor independently, it is often critical to identify the interaction effect between the factors.

A $2^4$ full factorial design was adopted for the present study with four identified parameters having two levels. The parameters influencing geopolymerization were taken as independent variables and the compressive strength of mortar cube is taken as dependent variable. Higher and lower levels of the parameters for full factorial design are tabulated in Table.4. “-” and “+” denote the low and high levels of a factor, respectively. The influencing parameters; molarity of NaOH, sodium silicate to sodium hydroxide ratio, alkali activator to binder ratio and elevated curing temperature are designated as A, B, C and D respectively.
Table 4. Factors and levels considered in Factorial design.

| Parameter                          | Factor notation | Higher level (+1) | Lower level (-1) |
|------------------------------------|-----------------|-------------------|------------------|
| Molarity of NaOH                   | A               | 12M               | 10M              |
| Sodium silicate to Sodium hydroxide ratio | B               | 2.5               | 2                |
| Alkali activator to Binder ratio   | C               | 0.8               | 0.6              |
| Elevated curing temperature        | D               | 65°C              | 55°C             |

2.4.1 Main effects of each independent factor

The main effects of each factor on compressive strength obtained from the statistical analysis are shown in Table 5.

Table 5. Main effects of factors

| Parameter (Factor)                          | Factor notation | Main effect of parameter (factor) on compressive strength (N/mm²) |
|---------------------------------------------|-----------------|------------------------------------------------------------------|
| Molarity of NaOH                            | A               | 7.48                                                             |
| Sodium silicate to Sodium hydroxide ratio   | B               | 1.78                                                             |
| Alkali activator to Binder ratio            | C               | 7.43                                                             |
| Elevated curing temperature                 | D               | 4.16                                                             |

From the Table 5, it is clear that the higher value of main effect of factor was observed with factor A and factor C, which means the highest effects on compressive strength was with molarity of NaOH and alkali activator to binder ratio. The parameter sodium silicate to sodium hydroxide ratio has the least effect among the four factors.

Main effect plots are drawn to visualize the effects. Plots with steeper slopes show the higher influence of the confirmed effects and hence more impact on development of compressive strength. The lines representing the influencing factors, molarity (Fig.4.a) and A/B ratio (Fig.4.c) are steeper than lines representing the other factors.
Fig. 4. Interaction effect between the independent factors

2.4.2 Interaction effect between the independent factors

The interaction effect between the independent factors is shown in Table 6. From the table, it is clear that the value of interaction effect between all parameters are negligible compared to the main effect of parameters on compressive strength.

Table 6. Interaction effects between the factors

| Interaction of parameters | AB   | AC   | AD   | BC   | BD   | CD   | ABC  | ACD  | BCD  | ABD  | ABCD |
|---------------------------|------|------|------|------|------|------|------|------|------|------|------|
| Interaction effect        | -0.14| 1.41 | 1.43 | -0.69| 0.13 | -0.02| -1.17| -1.89| -0.79| 0.86 | 0.58 |
| of parameters on compressive strength (N/mm²) |      |      |      |      |      |      |      |      |      |      |      |

2.4.3 Summary of ANOVA

ANOVA was performed and it is observed that the effect of interaction between the parameters is not significant. This supports the negligible value of interaction effect presented in Table 6. Hence they are taken together as error. The details of ANOVA are shown in Table 7. Here the main effects of molarity (Factor A), A/B ratio (Factor C) and enhanced temperature (Factor D) are significant. But SS/SH ratio (Factor B) is not significant at 5% level of significance. These results are confirmed by the findings of the extended experiments [19].
Table 7. ANOVA for the experiment with dependent variable: Compressive strength in N/mm²

| Parameter | Sum of Squares | df | Mean Square | F Value | Significant. |
|-----------|----------------|----|-------------|---------|--------------|
| A         | 224.026        | 1  | 224.026     | 55.019  | 0            |
| B         | 12.727         | 1  | 12.727      | 3.126   | 0.105        |
| C         | 221.043        | 1  | 221.043     | 54.286  | 0            |
| D         | 69.181         | 1  | 69.181      | 16.990  | 0.002        |
| Error     | 44.790         | 11 | 4.072       |         |              |
| Corrected Total | 571.766 | 15 |             |         |              |

3. Conclusion

The optimized mix proportion for geopolymer binder from terracotta roof tile waste is arrived based on the experimental investigations is at 12M molarity, 2.5 SS/SH ratio, 0.8 A/B ratio and 24 hours curing at 65°C. The significance of the influencing parameters in the geopolymerization reaction was identified by Statistical analysis. In the factorial design, the influence of the parameters such as molarity of sodium hydroxide, alkali activator to binder ratio and curing at enhanced temperature on geopolymerization has been proved as significant where as influence of sodium silicate to NaOH solution ratio was insignificant at 5% level of significance. In addition interaction effect among the parameters were also carried out and found to be negligible.

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Prof. S. Usha obtained her B.Tech degree in Civil Engineering from College of Engineering, Trivandrum under Kerala University in the year 1986 and M.Tech in Computer Aided Structural Engineering from Mar Athanasius College of Engineering under M.G. University in 2007. She is pursuing her Ph.D from Cochin University of Science & Technology. She has 13 years of industrial and 12 years of teaching experiences. She has published 10 research papers in reputed national journals and conferences. She is life time member of ISTE, ICI and FIE from Institution of Engineers (India).