Development of Detailed Mix Design Methodology for Low Calcium Fly Ash Based Geopolymer Concrete Incorporating OPC and Crumb Rubber

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Abstract: This experimental study proposes a systematic mix-design procedure to develop rubberized geopolymer concrete (RGPC). The developed method is meant to identify the mix ratios for the production of high-strength, low-calcium fly ash-based geopolymer concrete, with OPC as a supplementary binder and crumb rubber as a partial replacement for the fine aggregates. The binder (80% fly ash + 20% OPC) content (350, 375, and 400 kg/m^3), crumb rubber percentage (0, 5, 10, and 15%), and NaOH molarity (8, 10, and 12 M) are identified as key variables, with the focus on attaining the targeted compressive strength and workability under heat curing (60 °C). Thirty-six mix designs were tested for their compressive strength after 7 and 28 days, and their graphical relationship with the chosen variables is presented (CR-GPC graphs). A trial experiment with an example is performed to establish the validity of the developed mix-design procedure. It was found that the targeted compressive strength and slump of the rubberized GPC can be achieved with conviction.

Keywords: geopolymer concrete; low-calcium fly ash; OPC; crumb rubber; mix design; CR-GPC graphs; high-strength

1. Introduction

Concrete is the most typically used construction material around the world. The essential components of ordinary concrete are OPC and natural aggregates. In the Indian context, cement consumption stands at 329 million metric tonnes for 2022 and is estimated to keep increasing by approximately 7–8% in the coming years [1]. Cement production depletes natural resources and causes environmental pollution, which has led to a new line of research interest—exploring other building materials with cement-like properties [2–9]. Geopolymers have an adhesive property that has been used to bind the mineral aggregates to produce an alternative to conventional OPC concrete. The geopolymers are given preference over OPC due to their low production cost, low energy consumption, lower carbon footprint, and their sustainability. Studies have shown that the development of geopolymer concrete with a high compressive strength of more than 45 MPa is generally achievable [10–12]. Durability-wise, the geopolymer performed better than the standard concrete when subjected to a sulphate attack, chloride penetration, and carbonation [13–16]. The geopolymer binders have shown their potential to become viable, eco-friendly alternative binders because their industrial by-products, such as fly ash (FA), ground granulated slag (GGBS), and rice husk ash (RHA), are utilised as cementitious precursors in its synthesis [17]. These waste materials otherwise become a significant concern for the environment, regarding their storage and disposal. Using geopolymer as a cement alternative can cut greenhouse gas emissions by 44–64%, reduce the carbon footprint, and improve the durability of mortar or concrete [18].

According to the Central Electricity Authority, India (CEAI) [19], coal-fired thermal plants generate a significant amount of low-calcium fly ash. Currently, the Indian cement
industry only utilises about 20% of the fly ash generated annually [20,21]. Thus, fly ash-based geopolymer binder has excellent scope in India [22]. Indian fly ash has a low calcium content (less than 10%), due to which the related geopolymer binder exhibits a slower rate of strength development than OPC concrete [23]. The integrity of the low-calcium, fly ash-based geopolymer’s microstructure could be improved by employing additives rich in calcium [24]. The improved microstructure could reduce the porosity and permeability of the geopolymer mortar and concrete.

The mechanical properties of fly ash-based geopolymer are comparable to those of OPC [25,26]. Furthermore, the performance of the low-calcium fly ash geopolymer is superior to the OPC concrete in terms of durability properties [27,28] and fire resistance [29]. The performance of the GPC can be further enhanced by employing certain additives. For example, Mehta and Siddique (2017) [24] demonstrated that the integrity of the geopolymer microstructure could be improved by partially replacing the fly ash with OPC at various replacement levels. The improved microstructure resulted in a reduction of water absorption, porosity, and sorptivity of geopolymer concrete.

The role of geopolymer concrete as a sustainable structural material can be further improved by reducing the use of natural aggregates. The potential of alternative materials, such as rubber and recycled aggregates, in the partial or total replacement of the fine and coarse aggregates in conventional concrete, has been an area of previous research interest. Rubber aggregates are mainly manufactured from scrap tires. India produces over 6% of the global waste tires every year [30]. Dumping waste tires in open spaces is an environmental health issue, as rubber is non-biodegradable. Although using crushed tires in concrete makes them recyclable, rubber aggregates have been reported to decrease the mechanical strength and increase the porosity of concrete [31,32]. Despite the drawbacks, the incorporation of rubber aggregates has been reported to improve the ductility, impact resistance, toughness, and resistance to the cyclic freezing and thawing of concrete [33]. In addition to the advantages mentioned above, a decrease in the thermal expansion and density of the concrete was also observed [34,35].

Despite the numerous advantages of GPC, it has not been fully utilised in the concrete industry, because geopolymer concrete still suffers from inconsistent material properties and a limited availability of standard design procedures. The previous research proposed a mix-design technique specific for the particular materials and conditions, which cannot be treated as a standard method. Furthermore, various research on rubberized GPC selected mix proportions arbitrarily based on the available literature, and no study was undertaken to develop a mix design specific for RGPC. This study tackles the identified research gap and develops a mix-design guideline for fly ash-based geopolymer concrete, which is unique due to the use of OPC as the supplementary binder and the incorporation of crumb rubber as a partial replacement of the fine aggregates.

A trial experiment established the validity of the developed mix-design procedure to calculate the mix proportions for the rubberized GPC with confidence to achieve the targeted compressive strength (30–60 MPa) and slump (75–140 mm).

2. Review of Mix Design Methods and Their Limitations

Luhar et al. [32] evaluated the mechanical strength properties and abrasion resistance of fly ash-based GPC, employing rubber fibers as a partial substitute for the fine aggregate mass (10, 20 and 30%). The GPC mix proportions by mass were calculated using the Taguchi method and the previous study by Rangan [36]. The GPC design parameters (NaOH molarity, alkaline liquid/fly ash ratio, aggregate percentage, and water content) were kept constant, and their effect on the properties of the rubberized GPC were not examined. As the rubber fiber replacement was done by weight, the density of the geopolymer concrete was fixed at 2500 kg/m³, which defeats the advantage of using rubber aggregates to produce lightweight GPC. Furthermore, the properties of the fresh RGPC, such as its workability, were not studied. Luhar et al. [32] further compared the performance of rubberized GPC with rubberized OPC and concluded that the RGPC was better, but the
compressive strength decreased with increasing the rubber fiber replacement, and no suggestions were made to overcome the same.

Yossuf et al. [37] developed 10 rubberized GPC mixes and analyzed the effect of the fly ash and slag ratio, curing method, and mixing procedures on the compressive strength, drying shrinkage, water absorption, surface abrasion, and carbonation properties. The GPC mix design was done along the lines of the OPC mix guidelines. This study lacked significance, as irrelevant parameters were assumed as variables. Furthermore, very few GPC mixes were examined and the rubber replacement percentage of the fine aggregates was kept constant (20%) in all the mixes.

Zhong et al. [38] tested the workability and mechanical properties of fly ash–slag mortar with crumb rubber (5, 10%, and 15% replacement by volume of fine aggregate) and steel fiber reinforcement (0.5% and 1.0% by volume). The FA/GGBS ratio and alkaline/binder ratio were set as constants, based on the previous research [39]. Furthermore, the sodium hydroxide molarity (10 M) used in this study was also fixed. Although the workability of the GPC prepared in this study decreased with the rubber and fiber addition, no course of action was recommended to amend it.

Azmi et al. [40] explore the effect of crumb rubber (0, 5, 10, 15, and 20% by volume of fine aggregates) on the compressive strength of fly ash-based geopolymer concrete. The details of the mix-design proportions were not mentioned, as the alkaline activator-to-fly ash and the NaOH-to-Na$_2$SiO$_3$ ratios were fixed at 0.4 and 0.5, respectively. The author observed that the compressive strength gain rate decreased for the increased amount of crumb rubber in the mixture. This study identified the scope of adding a fast-reacting cementitious binder to the pozzolanic precursor in the rubberized GPC.

Park et al. [31] was the first to perform a comprehensive research study on GPC with rubber aggregates and attempted to investigate the effect of various design parameters on the compressive strength development of rubberized GPC having different crumb rubber percentages (5, 10, 15, and 20% by fine aggregates volume). This study selected the sodium hydroxide molarity (8 and 14 M), aggregates size (9.5 and 16 mm), rubber content, and calcium percentage in the fly ash (14.14, 9.42, and 1.29%) as the effective factors to prepare a total number of 38 design mixes. This research was limited to a 7-day trial of the compressive strength properties of the hardened concrete.

It can be gathered from the above literature that there cannot be a specific procedure for the development of rubberized GPC. Hence, it is necessary to evaluate the effect of all the essential GPC design parameters on the rubber aggregates’ performance in the fresh and hardened states. Therefore, in this study, an attempt was made to propose a mix-design procedure that covers the research gaps of the earlier proposed methods. In this research, the emphasis was on developing an RGPC mix design by targeting the desired strength and workability at heat curing.

3. Material Properties

3.1. Fly Ash

Low-calcium fly ash (FA) was chosen as the primary precursor in this study, and it endows GPC with its inherent binding properties. Fly ash procured from the Thermal power plant in the Jhajjar district of Haryana, India, met the physical and chemical requirements of IS 3812 (Part 1) [41] to be classified as a pozzolanic material. The physical and chemical characteristics of the FA are presented in Table 1.

An XRD analysis also confirms the presence of amorphous silica in the fly ash, as the presence of quartz, mullite, mellite, and calcite can be seen in Figure 1a. The SEM image in Figure 1b confirms the spherical shape of the FA particles as reported in the literature.
Table 1. Characteristics of fly ash.

| Physical Characteristics of Fly Ash | Chemical Composition of Fly Ash |
|-------------------------------------|---------------------------------|
| Characteristic                      | Chemical Composition            | Weight (%) |
| Specific density                   | Total silica (SiO$_2$)           | 60.17      |
| Blaine’s fineness (m$^2$/kg)       | Alumina (Al$_2$O$_3$)            | 21.66      |
| Particles retained on 45 micron IS sieve (wt.%) | Iron Oxide (Fe$_2$O$_3$)      | 6.33       |
| Mean particle size (µm)            | Calcium Oxide (CaO)              | 7.57       |
| Color                              | Total Sulfur (SO$_3$)            | 1.15       |
|                                    | Magnesium Oxide (MgO)            | 0.69       |
|                                    | Available alkali (Na$_2$O)        | 0.31       |

Figure 1. XRD spectrum and SEM image of fly ash. (a) XRD spectrum of fly ash; (b) SEM image of fly ash.

3.2. OPC

The OPC-43 grade cement conforming to IS 8112 [42] was acquired from the local market and adopted as the secondary binder. The results of the physical tests performed and chemical compositions of the OPC are tabulated in Table 2. The fineness test of the OPC showed that the fly ash is more refined than the cement. The initial setting time of cement was 35 min, much shorter than the time taken by a usual geopolymer reaction. This allows the fly ash particles to group around the cement solids and fill the voids after the initial stages of the cement hydration. The final setting-time of 565 min provides ample time for the activated fly ash particles to react with the cement hydration products. The compressive strength of the OPC-43 cement after 28 days is 47.31 MPa, which would provide the geopolymer binder with a high early-age strength. Because of the high calcium content of the OPC (63.44%), it stimulates the creation of additional calcium (Ca) compounds, such as calcium silicate hydrate (CSH) and calcium aluminate silicate hydrate (CASH) gels, which contribute to the strength gain [43] of the geopolymer binder.

3.3. Sodium Hydroxide and Sodium Silicate

Sodium hydroxide was chosen as one of the alkaline solutions for activating the fly ash particles, which was used in combination with sodium silicate. NaOH solutions of 8, 10, and 12 M were prepared by dissolving NaOH pellets in tap water. The laboratory reagent-grade NaOH pellets with 98.84% purity were acquired from a local chemical store. The NaOH solution was prepared a day before mixing it with the sodium silicate solution, and it was then kept at room temperature for 24 h to allow the excessive heat to be released. This study used a viscous syrup of sodium silicate as the other alkaline activator. The
cloudy and translucent Na$_2$SiO$_3$ solution with specific gravity at 20 °C as 52 °Be’ or 1.559 and an alkaline modulus ratio (SiO$_2$/Na$_2$O) of 2.20 was sorted from a local commercial producer. The Na$_2$SiO$_3$ solution was mixed for about 5 min with the NaOH solution to prepare the alkaline-activator solution.

### Table 2. Physical properties and chemical composition of OPC.

| Physical Property                     | Value  |
|--------------------------------------|--------|
| Fineness (m$^2$/kg)                  | 320    |
| Initial setting time (min)           | 35     |
| Final setting time (min)             | 565    |
| 28-day compressive strength (MPa)    | 47.31  |

| Chemical Composition                  | Weight (%) |
|--------------------------------------|------------|
| Silica (SiO$_2$)                      | 19.21      |
| Alumina (Al$_2$O$_3$)                 | 7.64       |
| Iron Oxide (Fe$_2$O$_3$)              | 5.36       |
| Total Sulphur (SO$_3$)                | 3.21       |
| Calcium Oxide (CaO)                   | 63.44      |
| Potassium Oxide (K$_2$O)              | 0.78       |
| Sodium Oxide (Na$_2$O)                | 0.36       |
| Loss on Ignition (LOI)                | 1.91       |

3.4. Superplasticizer

In the current study, the GPC prepared had a high viscosity due to the presence of the viscous alkaline-activator solution in the initial stages. The incorporation of the GF and CR further reduces the GPC flowability [44]. So, polycarboxylate ether conforming to IS 9103 [45] was used as a water-reducing superplasticizer to improve the workability of the fresh GPM mix.

3.5. Coarse Aggregates

Shop-available coarse aggregates conforming to the requirements of IS 383 [46] were tested. The grading curve is shown in Figure 2, and physical properties of the coarse aggregates are tabulated in Table 3.

![Figure 2. Grading curve of coarse aggregate.](image-url)
Table 3. Physical properties of coarse aggregates.

| Property           | Coarse Aggregates |
|--------------------|-------------------|
| Specific Gravity   | 2.66              |
| Fineness Modulus   | 7.10              |
| Water Absorption   | 0.87%             |

3.6. Fine Aggregates and Crumb Rubber

Natural sand from the plains of the Yamuna River, India, was utilized as the fine aggregates, which met the guidelines of IS 383 [46]. A sieve analysis was performed to examine the grading of the fine aggregates, following the provisions of IS 2386 [47], and the particle size distribution (PSD) curve is presented in Figure 3. The fine aggregates had a maximum size of 2.36 mm, as it can be observed from Figure 3 that 100% of the particles pass through a 4.75 mm sieve. The specific gravity and fineness modulus of the fine aggregates, respectively, was 2.65 and 2.8, as shown in Table 4.

![PSD curve of fine aggregates and CR.](image)

Table 4. Physical properties of fine aggregates.

| Properties          | Fine Aggregates | CR |
|---------------------|-----------------|----|
| Specific density    | 2.65            | 1.13|
| Bulk density (kg/m^3)| 1656            | 502 |
| Water absorption (%)| 1.4             | -   |
| Fineness modulus    | 2.8             | 3.1 |

The crumb rubber was procured from a local supplier in Bahadurgarh, India, and was manufactured from recycled scrap truck tires, as they contain a high quantity of natural rubber. The cryogenic method was applied to process the CR particles into the required regular shape and size for this study (75–425 µm), as shown in Figure 3. With a specific gravity of 1.13, the CR particles were partially used to replace the fine aggregates. The results presented in Table 4 and Figure 3 infer that CR particles could be used to fill the voids within the fine aggregates. Furthermore, the CR particles’ surface was water-repellent and resistant to the corrosive action of alkali and acids [48,49].
4. Proposed Method for Designing Rubberized GPC Using Fly Ash and OPC

This study strives to develop a mix-design methodology for OPC–fly ash-based RGPC in logical and simple terms. By ascertaining the effect of various design parameters on the strength of RGPC, it can be produced economically. The proposed design method also provides flexibility in selecting the range of design parameters (fly ash content, NaOH molarity, crumb rubber percentage) for the targeted performance of the concrete in terms of strength and workability.

Further, as established in the literature, OPC-infused GPC cured at elevated temperature achieves a majority of its final strength at an early age, hence a relationship equation is derived between the 28-day and 7-day compressive strengths, as shown in Figure 5.

The design procedure adopted in this study for preparing the rubberized GPC is discussed in detail in the following sub-sections.

4.1. Selection of Binder Content

In this study, three amounts of binder content (350, 375, and 400 kg/m$^3$) are selected by drawing guidance from the available literature on low-calcium, fly ash-based GPC, amalgamated with calcium-rich precursors.

4.2. Fixing the Alkaline Activator Liquid (AAS) to Binder Ratio

Selecting an appropriate alkaline-activator liquid (AAL) content is a crucial step in the design of any GPC and is dependent on the binder content used in the mix. It has been reported that an AAL/binder ratio between 0.3 and 0.6 is sufficient for practical usage [50]. However, a value of 0.45 was selected in this study to prepare the CR–GPC graphs, because the previous literature on GPC suggests that low values of the AAL/binder are not able to completely dissolve the geopolymer precursor.

4.3. Calculation of AAL Content

The AAL content was calculated using the binder content and the AAL/binder ratio.

\[
\text{AAL content} = 0.45 \times \text{Binder content}
\]

4.4. Fixing Sodium Silicate/Sodium Hydroxide Ratio

The sodium silicate-to-sodium hydroxide (Na$_2$SiO$_3$/NaOH) mass ratio has a critical impact on the geopolymerization reaction. From the available literature, it has been deduced that empirical values between 2.3 and 2.8 are feasible for GPC production [51–54]. However, a middle value of 2.5 was fixed for this study to keep the production cost of the GPC in check. The individual weights of the NaOH and Na$_2$SiO$_3$ solutions are calculated from Equations (1) and (2).

\[
\begin{align*}
\frac{\text{AAL}}{\text{Binder}} &= \frac{\text{Sodium Silicate solution} + \text{Sodium hydroxide solution}}{\text{Fly ash} + \text{OPC}} = 0.45 \quad (1) \\
\frac{\text{Sodium Silicate}}{\text{Sodium hydroxide}} &= 2.5 \quad (2)
\end{align*}
\]

from which the NaOH solution weight = AAL/3.5, and the Na$_2$SiO$_3$ solution weight = 2.5 × the sodium hydroxide solution weight.

4.5. Fixing of Water Content in GPC and Calculation of Extra Water

The total water present in the GPC system decides the mixing efficiency of the ingredients and the rate of the geopolymerization reaction. The water content has a similar role in GPC production as in conventional concrete mix. The total water is the sum of the water mass present in the Na$_2$SiO$_3$ and NaOH solution and the weight of the additional free water mixed later. The water content is calculated with the help of the W/GPB ratio, where the geopolymer binder solids (GPB) are total weight of the fly ash, OPC, NaOH solids, and
Na$_2$SiO$_3$ solids. Generally, a higher water content results in an increased workability but, during heat curing, the excess pore water evaporates, thus damaging the integrity of the GPC matrix. Therefore, a $W_{GPB}$ value of 0.27 was selected to maintain a balance between the desired workability and the hardened GPC matrix porosity [51–54]. The additional free water quantity was calculated using Equation (3).

$$\frac{W}{GPB} = \frac{WSH + WSS + W_{Extra}}{OPC + FA + NaOH solids + Na2SiO3 solids} = 0.27$$  \hspace{1cm} (3)

where $W_{SH}$, $W_{SS}$, and $W_{Extra}$ is the water in the sodium hydroxide and sodium silicate solution and the additional free water required in the GPC mix, respectively.

4.6. Superplastizer Content

A superplasticizer (2% of binder content) was added to the GPC mix in order to achieve a workable slump without affecting the compressive strength of the concrete.

Superplasticizer weight = 0.02 $\times$ Binder content

4.7. Determination of Coarse and Fine Aggregates Content

In this research, the aggregates were used in a saturated surface-dry (SSD) condition. Further, the total aggregates account for the remaining GPC volume. The coarse and fine aggregates were mixed in a 70:30 ratio by weight. The individual weight content of the coarse and fine aggregates was calculated using Equations (4) to (6).

Total GPC volume (1 m$^3$) = $V_{Binder} + V_{AAL} + V_{Extra water} + V_{Air} + V_{Plasticizer} + V_{Total aggregates}$  \hspace{1cm} (4)

$V_{Total aggregates} = \frac{W_{Coarse aggregates}}{S.G. Coarse aggregates} + \frac{W_{Fine aggregates}}{S.G. Fine aggregates}$  \hspace{1cm} (5)

where

$$W_{Coarse aggregates} = (7/3) \times W_{Fine aggregates}$$  \hspace{1cm} (6)

4.8. Calculation of Crumb Rubber Content and Revised Fine Aggregates Content

Crumb rubber was used to replace the fine aggregates by volume in this study. The replacement percentages employed were 0, 5, 10, and 15%. Crumb rubber weight content was calculated by using Equations (7) to (8).

$$V_{Crumb rubber} = \text{Percentage replacement} \times V_{Fine aggregates}$$  \hspace{1cm} (7)

$$W_{Crumb rubber} = S.G. - Crumb rubber \times V_{Crumb rubber}$$  \hspace{1cm} (8)

The revised fine aggregates weight ($W'_{Fine aggregates}$) was calculated from Equation (9).

$$W'_{Fine aggregates} = (V_{Fine aggregates} - V_{Crumb rubber}) \times S.G. - Fine aggregates$$  \hspace{1cm} (9)

4.9. Development of CR–GPC Compressive Strength and Slump Graphs

The CR–GPC graphs were developed using the design-mix proportions (Table 5) of this investigation and form the basis of the developed mix design. These graphs (Figure 4a–d) establish the compressive strength and slump relationships with the binder content (350, 375, and 400 kg/m$^3$) and NaOH molarity (8, 10, and 12 M) under temperature-curing at 60 °C. Heat curing is suitable for achieving high strength in GPC, however, temperature above 60 °C has insignificant effect on geopolymerisation rate. Furthermore, considering the economical sustainability of the proposed method, 60 °C was selected for curing purpose. The workability of the fresh GPC was measured using the standard slump test [55], and the compressive strength test was performed as per IS 516 [56].
### Table 5. Mix proportions used in this study (by weight).

| Mixture | FA  | OPC  | CR  | Sand | C_A  | M:NaOH | NaOH | Na2SiO3 | Extra Water | SP  | Curing Temp. (°C) |
|---------|-----|------|-----|------|------|---------|------|---------|-------------|-----|------------------|
| B1CR0   | 280 | 70   | -   | 532.7| 1242.9| 8/10/12 | 45.0 | 112.5   | 25.3        | 7   | 60               |
| B2CR0   | 300 | 75   | -   | 515.1| 1201.8| 8/10/12 | 48.2 | 120.5   | 27.1        | 7.5 | 60               |
| B3CR0   | 320 | 80   | -   | 497.5| 1160.7| 8/10/12 | 51.4 | 128.6   | 28.9        | 8   | 60               |
| B1CR5   | 280 | 70   | 11.36| 506.0| 1242.9| 8/10/12 | 45.0 | 112.5   | 25.3        | 7   | 60               |
| B2CR5   | 300 | 75   | 10.98| 489.3| 1201.8| 8/10/12 | 48.2 | 120.5   | 27.1        | 7.5 | 60               |
| B3CR5   | 320 | 80   | 10.61| 472.6| 1160.7| 8/10/12 | 51.4 | 128.6   | 28.9        | 8   | 60               |
| B1CR10  | 280 | 70   | 22.71| 479.4| 1242.9| 8/10/12 | 45.0 | 112.5   | 25.3        | 7   | 60               |
| B2CR10  | 300 | 75   | 21.96| 463.6| 1201.8| 8/10/12 | 48.2 | 120.5   | 27.1        | 7.5 | 60               |
| B3CR10  | 320 | 80   | 21.21| 447.7| 1160.7| 8/10/12 | 51.4 | 128.6   | 28.9        | 8   | 60               |
| B1CR15  | 280 | 70   | 34.07| 452.8| 1242.9| 8/10/12 | 45.0 | 112.5   | 25.3        | 7   | 60               |
| B2CR15  | 300 | 75   | 32.94| 437.8| 1201.8| 8/10/12 | 48.2 | 120.5   | 27.1        | 7   | 60               |
| B3CR15  | 320 | 80   | 31.82| 422.8| 1160.7| 8/10/12 | 51.4 | 128.6   | 28.9        | 8   | 60               |

* CR—crumb rubber, C_A—coarse aggregates, M—molarity, TAS—total alkaline solution, SP—Superplasticizer, all quantities are taken in kg/cubic meters.

**Figure 4.** Compressive strength and slump relationships with binder content and molarity at 60 °C curing temperature. Note: CR5-GPC-28D-60: Rubberized Geopolymer Concrete with 5% CR, 28 curing days, and at 60 °C degrees curing temperature.
To better understand the strength development rate of the OPC–fly ash RGPC, a relationship is established between its 7-day and 28-day compressive strength, as shown in Figure 5. It can be observed from the below figure that there is very little difference in both strengths, which demonstrates that the prepared RGPC developed a high early-age strength.

![Figure 5](image-url)

**Figure 5.** Relationship between 7-day and 28-day compressive strength of various design RGPC mixes.

### 5. Proposed Procedure for Sample Preparation

The suggested procedure for the GPC samples preparation is discussed below:

1. The mixing procedure was performed at room temperature (25–27 °C). First, the dry materials, such as the FA, OPC, CR, and sand, were mixed to achieve a uniform distribution. Then, the alkaline-activator solution of NaOH and Na$_2$SiO$_3$ was progressively added to the mix, followed by the extra water and superplasticizer.

2. The fresh GPC of a particular mix design was cast into standard cube molds (150 × 150 × 150 mm), then compacted and immediately covered with a polyvinyl sheet to avoid water evaporation.

3. After the casting, the specimens were placed in an oven for steam curing at 60 °C for 24 h, and the relative humidity was maintained at approximately 60%. After the steam curing, the samples were de-molded and allowed to cool at room temperature (25–27 °C) until the testing.

### 6. Experimental Verification of the Mix Methodology

The proposed design method for the rubberized GPC is explained and validated with a trial experiment and the calculation of the mix proportions is explained through an example.

Assuming the required compressive strength and workability for the fly ash-based rubberized GPC is 35 MPa, 90 mm, and 40 MPa, 90 mm:

First, the target mean strength has been calculated, as per IS 456 specifications [56]

\[
1.65 \times S + F_{ck} = F_{ck}',
\]

where $F_{ck}$ is the characteristics compressive strength; $F_{ck}'$ is the target mean compressive strength; and $S$ is the respective standard deviation.
To achieve the desired target strength and slump, several combinations of the binder content, NaOH molarity, and crumb rubber percentage could be selected from the CR–GPC graphs presented in Figure 4.

Target strengths = 43.25 and 48.25 MPa

Firstly, we looked to design a GPC mix that achieves the target strength and slump values for the maximum-possible crumb rubber utilization. Secondly, we looked to design an economical mix, which can be achieved by employing the minimum feasible alkaline solution content and low molarity NaOH solution.

So, as per the first priority of the design criteria, the required target strength of 43.25 and the 90 mm slump can be achieved simultaneously and easily located on Figure 4d (CR15–GPC). The located region provides different mix-design combinations with different binders and NaOH molarities.

The second priority was to select the lowest-possible binder content, as the AAL content is directly proportional to the binder content. There are two possible options for the binder content, 375 and 395 kg/m$^3$, to achieve the target strength of 43.25 MPa.

However, the binder content of 375 kg/m$^3$ does not provide the desired slump value. Therefore, either the superplasticizer content is increased above 2% until the required slump is achieved for this binder content, or the other option of 395 kg/m$^3$ is selected. From the graph in Figure 4d, it can be seen that the binder content of 395 kg/m$^3$ readily satisfies both the strength and workability parameters. The design calculations for the trial mixes-35 are presented in Table 5, with the expected and actual strength achieved.

The required target strength of 48.25 MPa cannot be located on Figure 4d (CR15-GPC), as desired by the first priority of the design criteria. Therefore, we move to the second-best option of the 10% CR graphs in Figure 4c (CR10-GPC). As can be seen from Figure 4c, the binder content of 380 kg/m$^3$ with 12 M NaOH produces the desired results. However, this mix requires a high AAL content and high molarity, which increases the preparation cost of the GPC mix. Therefore, we further look for other available options in the 5% CR graphs, Figure 4b (CR05-GPC). In this graph, the binder content and molarity combinations of 360, 375, and 390 kg/m$^3$ with 12 M, 10 M, and 8 M NaOH, respectively, are expected to produce the desired results. The design calculations for the trial mixes-40 are presented in Table 5, with the expected and actual strength achieved.

The solved example (all units in kg/m$^3$) for the design mix for the experimental mix, EM-40, for the binder content of 380 kg/m$^3$ and 12 M NaOH:

1. Fly ash content = 0.8 $\times$ 380 = 304
2. AAL content = 0.45 $\times$ 380 = 171
3. NaOH solution = 171/3.5 = 48.85
   
   NaOH solids = 0.383 $\times$ 48.85 = 18.71
   NaOH water = 48.85 − 18.71 = 30.14
4. $\text{Na}_2\text{SiO}_3$ solution = 2.5 $\times$ 48.85 = 122.15
   
   $\text{Na}_2\text{SiO}_3$ solids = 0.486 $\times$ 122.15 = 59.36
   $\text{Na}_2\text{SiO}_3$ water = 122.15 − 59.36 = 62.78
5. GPB solids = 380 + 18.71 + 59.36 = 458.07
6. Extra water = (0.27 $\times$ 458.07) − (30.14 + 62.78) = 123.68 − 92.92 = 30.76
7. Superplasticizer = 0.02 $\times$ 380 = 7.6
(8) Volume of the total aggregates in m$^3$ was calculated by using Equation (4), as follows:

$$V_{\text{total aggregates}} = 1 - \left( \frac{V_{\text{Binder}} + V_{\text{AAL}} + V_{\text{Extra water}} + V_{\text{Air}} + V_{\text{Plasticizer}}}{1000} \right) - (0.02)$$

$$= 1 - \left( \frac{W_{\text{Fly ash}} + W_{\text{OPC}} + W_{\text{NaOH}} + W_{\text{Na$_2$SiO$_3$}} + W_{\text{Water}} + W_{\text{Plasticizer}}}{1000} \right) - (0.02)$$

$$= 1 - \left( \frac{304 + 76 + 48.85 + 30.76 + 7.6 + 1.21}{1000} \right) - (0.02)$$

$$= 1 - \left( \frac{160 + 24.12 + 39.08 + 78.31 + 6.28}{1000} \right) - (0.02)$$

$$= 1 - \left( \frac{3.385}{1000} \right) - (0.02)$$

$$= 0.64145 \text{ m}^3$$

(9) Volume of the coarse and fine aggregates was calculated using Equations (5) and (6), as follows:

$$V_{\text{Total aggregates}} = \left( \frac{W_{\text{Coarse aggregates}}}{S.G_{\text{Coarse aggregates}}} + \frac{W_{\text{Fine aggregates}}}{S.G_{\text{Fine aggregates}}} \right) / 1000$$

$$= \left( \frac{7/3 \times W_{\text{Fine aggregates}}}{2.66} + \frac{W_{\text{Fine aggregates}}}{2.65} \right) / 1000$$

$$= 1.25 \times 10^{-3} \times W_{\text{Fine aggregates}}$$

Hence, $W_{\text{Fine aggregates}} = 511.52$ kg

$W_{\text{Coarse aggregates}} = \left( \frac{7}{3} \right) \times 511.52 = 1534.57$ kg

(10) Crumb rubber = $0.10 \times \left( \frac{511.52}{2.65} \right) \times 1.13 = 21.81$ kg

Fine aggregates (revised) = $0.9 \times 511.52 = 460.37$ kg

Table 6 shows the mix design quantities of different mixes as calculated by using the proposed method.

| Mix  | EM-35  | EM-35 | EM-40  | EM-40  | EM-40  | EM-40  |
|------|--------|--------|--------|--------|--------|--------|
| Target strength (MPa) | 43.25  | 43.25  | 48.25  | 48.25  | 48.25  | 48.25  |
| Target slump (mm) | 90     | 90     | 90     | 90     | 90     | 90     |
| OPC  | 300.00 | 316.00 | 304.00 | 288.00 | 300.00 | 312.00 |
| Coarse Aggregates | 1198.16 | 1169.11 | 1189.91 | 1222.95 | 1201.82 | 1181.21 |
| Fine aggregate | 436.47 | 425.81 | 458.96 | 497.92 | 489.31 | 480.92 |
| Crumb rubber | 32.84 | 32.04 | 21.75 | 11.17 | 10.98 | 10.79 |
| NaOH | 48.21 | 50.79 | 48.86 | 46.29 | 48.21 | 50.14 |
| Molarity[M] | 12 | 10 | 12 | 12 | 10 | 8 |
| Na$_2$SiO$_3$ | 120.54 | 126.96 | 122.14 | 115.71 | 120.54 | 125.36 |
| Extra water | 30.35 | 28.55 | 30.75 | 29.14 | 27.10 | 24.59 |
| Plastisizer | 7.50 | 7.90 | 7.60 | 7.20 | 7.50 | 7.80 |
| Expected compressive strength [MPa] | 43.75 | 43.5 | 48.5 | 48.5 | 48.75 | 48.5 |
| Tested compressive strength [MPa] | 44.43 | 45.08 | 49.35 | 48.93 | 49.51 | 49.77 |

From Table 6 it could be seen that the expected compressive strength of the mix EM-35 with binder content 375 and 395 kg/m$^3$ was 43.75 and 43.5 MPa as per the proposed design graphs. The experimental results shows the compressive strength of 44.43 and 45.08 MPa, respectively. The possible reasons for the variation in compressive strength could be the variation of concentration of NaOH, total binder content and aggregate content.

Whereas, in the case of EM-40 it was observed that similar compressive strength of 48.5 MPa, could be expected with 5 and 10% CR substitution. However, to achieve this binder content is to be increased from 360 to 380 kg/m$^3$. The binder content has direct relation with compressive strength. This is due to the fact that hydrophobic characteristic of rubber reduces the penetration of geopolymer gel in CR aggregate and results in insufficient
interface adhesion. Furthermore, for 5% CR, similar compressive strength could be expected if the binder content is increased from 375 to 390 kg/m³, and also, NaOH molarity is decreased from 10M to 8M. Furthermore, tested compressive strength of all experimental mixes was slightly higher than the expected results, which proves that the proposed method could be employed in practical applications.

7. Limitations of the Method

Though considerable strength, up to 47 MPa, can be achieved, even with the 15% CR addition, a decrease in the compressive strength of the rubberized GPC was observed with the increase in the CR addition. This drawback of the rubber aggregates could be counterbalanced by the use of a fiber reinforcement in the RGPC.

The effect of the AAL content and CR treatment on the properties of the fresh and hardened RGPC could also be explored.

8. Conclusions

Based on the data and observations presented above, the following conclusions can be made:

1. In this study, a mix-design methodology has been suggested for preparing the mix design for low-calcium, fly ash-based geopolymer concrete.
2. The uniqueness of the above methodology lies in the number of variable parameters and mix designs undertaken for analyzing their effect on the compressive strength and workability of the rubberized GPC.
3. The proposed mix design is simple and able to achieve the target strength with a high confidence level.
4. The OPC-supplemented GPC, incorporating a 15% crumb rubber replacement of the sand, is able to achieve a high, 7-day compressive strength of 43.26 MPa under heat curing.

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References

1. Sun, S. Cement Consumption Volume in India FY 2009–2022. 2022. Available online: https://www.statista.com/statistics/269322/cement-consumption-in-india-since-2004/ (accessed on 10 March 2022).
2. Saloni; Parveen; Lim, Y.Y.; Pham, T.M. Effective utilisation of ultrafine slag to improve mechanical and durability properties of recycled aggregates geopolymer concrete. Clean. Eng. Technol. 2021, 5, 100330. [CrossRef]
3. Saloni; Parveen; Lim, Y.Y.; Pham, T.M. Influence of Portland cement on performance of fine rice husk ash geopolymer concrete: Strength and permeability properties. Constr. Build. Mater. 2021, 300, 124321. [CrossRef]
4. Jindal, B.B.; Singhal, D.; Sharma, S.; Ashish, D.K.; Jangra, P. Improving compressive strength of low calcium fly ash geopolymer concrete with alccofine. Adv. Concr. Constr. 2017, 5, 17–29. [CrossRef]
5. Jangra, P.; Singhal, D.; Jindal, B.B. Preparation of Geopolymer Concrete (GPC) Using High-Silica Rice Husk Ash (RHA) Incorporating Alccofine. Adv. Sci. Eng. Med. 2017, 9, 370–376.
6. Saloni; Parveen; Lim, Y.Y.; Pham, T.M.; Negi, P. Performance enhancement of rubberised-alkali-activated-concrete utilising ultra-fine slag and fly ash. Clean. Mater. 2022, 4, 100080. [CrossRef]
7. Jangra, P.; Singhal, D.; Jindal, B.B.; Garg, A. Mechanical Properties of Ground Granulated Blast Furnace Slag Based Geopolymer Concrete Incorporating Alcofines with Different Concentration and Curing Temperature. Adv. Sci. Eng. Med. 2017, 9, 948–958.

8. Pradhan, S.S.; Mishra, U.; Biswal, S.K.; Jangra, P.; Pham, T.M.; Arora, S.; Lim, Y.Y. Effects of crumb rubber inclusion on strength, permeability, and acid attack resistance of alkali-activated concrete incorporating different industrial wastes. Struct. Concr. 2022, 1–15. [CrossRef]

9. Saloni; Parveen; Pham, T.M.; Lim, Y.Y.; Pradhan, S.S.; Jatin; Kumar. J. Performance of rice husk Ash-Based sustainable geopolymer concrete with Ultra-Fine slag and Corn cob ash. Constr. Build. Mater. 2021, 279, 122526. [CrossRef]

10. Neupane, K. High-Strength Geopolymer Concrete–Properties, Advantages and Challenges. Adv. Mater. 2018, 7, 15. [CrossRef]

11. Bakri, A.M.; Kamarudin, H.; Binhusain, M.; Nizar, I.K.; Rafiza, A.R.; Zarina. Y. Comparison of geopolymer fly ash and ordinary Portland cement to the strength of concrete. Adv. Sci. Lett. 2013, 19, 3592–3595. [CrossRef]

12. Ma, C.K.; Awang, A.Z.; Omar, W. Structural and material performance of geopolymer concrete: A review. Constr. Build. Mater. 2018, 186, 90–102. [CrossRef]

13. Chen, K.; Wu, D.; Xia, L.; Cai, Q.; Zhang, Z. Geopolymer concrete durability subjected to aggressive environments—A review of influence factors and comparison with ordinary Portland cement. Constr. Build. Mater. 2021, 279, 122496. [CrossRef]

14. Albitar, M.; Ali, M.S.M.; Visintin, P.; Drechsler, M. Durability evaluation of geopolymer and conventional concretes. Constr. Build. Mater. 2017, 136, 374–385. [CrossRef]

15. Lavanya, G.; Jegan, J. Durability Study on High Calcium Fly Ash Based Geopolymer Concrete. Adv. Sci. Eng. 2015, 2015, 731056. [CrossRef]

16. Jin, H.; Liu, J.; Jiang, Z.; Zhou, H.; Liu, J. Influence of the rainfall intensity on the chloride ion distribution in concrete with different levels of initial water saturation. Constr. Build. Mater. 2021, 281, 122561. [CrossRef]

17. Azad, N.M.; Samarakoon, S.M.S.M.K. Utilization of Industrial By-Products/Waste to Manufacture Geopolymer Cement/Concrete. Sustainability 2021, 13, 873. [CrossRef]

18. McLellan, B.C.; Williams, R.P.; Lay, J.; van Riessen, A.; Corder, G.D. Costs and carbon emissions for geopolymer pastes in comparison to ordinary Portland cement. J. Clean. Prod. 2011, 19, 1080–1090. [CrossRef]

19. Delhi, N. Report on Fly Ash Generation at Coal/Lignite Based Thermal Power Stations and its Utilization in the Country for the year 2016-17. Cent. Electr. Auth. 2017, 1–63.

20. No, P. Productivity, Technology and Environmental Logistics Related Issues—Bulk Transport, Cement Export, Cement Import and WTO. Available online: https://www.wto.org/english/res_e/booksp_e/wtr21_e/00_wtr21_e.pdf/ (accessed on 20 March 2022).

21. Liu, J.; Liu, J.; Huang, Z.; Zhu, J.; Liu, W.; Zhang, W. Effect of fly ash as cement replacement on chloride diffusion, chloride binding capacity, and micro-properties of concrete in a water soaking environment. Appl. Sci. 2020, 10, 6721. [CrossRef]

22. Rastogi, A.; Paul, V.K. A Critical Review of the Potential for Fly Ash Utilisation in Construction-Specific Applications in India. J. Environ. Res. Eng. Manag. 2020, 76, 65–75. [CrossRef]

23. Liu, J.; Hu, L.; Tang, L.; Zhang, E.Q.; Ren, J. Shrinkage behaviour, early hydration and hardened properties of sodium silicate activated slag incorporated with gypsum and cement. Constr. Build. Mater. 2020, 248, 118687. [CrossRef]

24. Mehta, A.; Siddique, R. Properties of low-calcium fly ash based geopolymer concrete incorporating OPC as partial replacement of fly ash. Constr. Build. Mater. 2017, 150, 792–807. [CrossRef]

25. Farhan, N.A.; Sheikh, M.N.; Hadi, M.N.S. Investigation of engineering properties of normal and high strength fly ash based geopolymer and alkali-activated slag concrete compared to ordinary Portland cement concrete. Constr. Build. Mater. 2019, 196, 26–42. [CrossRef]

26. Arora, S.; Jangra, P.; Pham, T.M.; Lim, Y.Y. Enhancing the Durability Properties of Sustainable Geopolymer Concrete Using Recycled Coarse Aggregate and Ultrafine Slag at Ambient Curing. Sustainability 2022, 14, 10948. [CrossRef]

27. Amran, M.; Debbarma, S.; Ozbakaloglu, T. Fly ash-based eco-friendly geopolymer concrete: A critical review of the long-term durability properties. Constr. Build. Mater. 2021, 270, 121857. [CrossRef]

28. Liu, J.; An, R.; Jiang, Z.; Jin, H.; Zhu, J.; Liu, W.; Huang, Z.; Xing, F.; Liu, J.; Fan, X.; et al. Effects of w/b ratio, fly ash, limestone calcined clay, seawater and sea-sand on workability, mechanical properties, drying shrinkage behavior and micro-structural characteristics of concrete. Constr. Build. Mater. 2022, 321, 126333. [CrossRef]

29. Zhao, R.; Sanjayan, J.G. Geopolymer and Portland cement concretes in simulated fire. Mag. Concr. Res. 2011, 63, 163–173. [CrossRef]

30. Mishra, L. Turning waste tyre into ‘green steel’. Hindu 2016, 1–5.

31. Park, Y.; Abolmaali, A.; Kim, Y.H.; Gahremannejad, M. Compressive strength of fly ash-based geopolymer concrete with crumb rubber partially replacing sand. Constr. Build. Mater. 2016, 118, 43–51. [CrossRef]

32. Luhar, S.; Chaudhary, S.; Luhar, I. Development of rubberized geopolymer concrete: Strength and durability studies. Constr. Build. Mater. 2019, 204, 740–753. [CrossRef]

33. Bala, A.; Gupta, S. Thermal resistivity, sound absorption and vibration damping of concrete composite doped with waste tire Rubber: A review. Constr. Build. Mater. 2021, 299, 123939. [CrossRef]

34. Aly, A.M.; El-Feky, M.S.; Kohail, M.; Nasr, E.S.A.R. Performance of geopolymer concrete containing recycled rubber. Constr. Build. Mater. 2019, 207, 136–144. [CrossRef]

35. Kaloush, K.E.; Way, G.B.; Zhu, H. Properties of crumb rubber concrete. Transp. Res. Rec. 2005, 1914, 8–14. [CrossRef]
36. Sumajouw, M.D.J.; Rangan, B.V. Low-Calcium Fly Ash-Based Geopolymer Concrete: Reinforced Beams And Columns By Faculty of Engineering Curtin University of Technology. GC3 Fac. Eng. Curtin Univ. Technol. 2006, 1–120.

37. Youssf, O.; Elchalakani, M.; Hassanli, R.; Roychand, R.; Zhuge, Y.; Gravina, R.J.; Mills, J.E. Mechanical performance and durability of geopolymer lightweight rubber concrete. J. Build. Eng. 2022, 45, 103608. [CrossRef]

38. Zhong, H.; Poon, E.W.; Chen, K.; Zhang, M. Engineering properties of crumb rubber alkali-activated mortar reinforced with recycled steel fibres. J. Clean. Prod. 2019, 238, 117950. [CrossRef]

39. Fang, G.; Ho, W.K.; Tu, W.; Zhang, M. Workability and mechanical properties of alkali-activated fly ash-slag concrete cured at ambient temperature. Constr. Build. Mater. 2018, 172, 476–487. [CrossRef]

40. Azmi, A.A.; Abdullah, M.M.A.B.; Ghazali, C.M.R.; Sandu, A.V.; Hussin, K. Effect of Crumb Rubber on Compressive Strength of Fly Ash Based Geopolymer Concrete. MATEC Web Conf. 2016, 78, 4–8. [CrossRef]

41. IS 3812 (Part 1); Pulverized Fuel Ash—Specification Part 1 for Use as Pozzolana in Cement, Cement Mortar and Concrete. Bureau of Indian Standard(BIS): New Delhi, India, 1989.

42. IS:8112; Specification for 43 Grade Ordinary Portland Cement. Bureau of Indian Standard(BIS): New Delhi, India, 1989.

43. Saloni; Parveen; Pham, T. Enhanced Properties of High-Silica Rice Husk Ash-Based Geopolymer Paste by Incorporating Basalt Fibers. Constr. Build. Mater. 2020, 245, 118422. [CrossRef]

44. Bisht, K.; Ramana, P.V. Evaluation of mechanical and durability properties of crumb rubber concrete. Constr. Build. Mater. 2017, 155, 811–817. [CrossRef]

45. IS 9103; Concrete Admixtures—Specification. BIS: New Delhi, India, 1999.

46. IS 383; Specification for Coarse and Fine Aggregates from Natural Sources for Concrete. BIS: New Delhi, India, 1970.

47. IS:2386 (Part I); Methods of Test for Aggregates for Concrete. BIS: New Delhi, India, 1963.

48. Bisht, K.; Ramana, P.V. Waste to resource conversion of crumb rubber for production of sulphuric acid resistant concrete. Constr. Build. Mater. 2019, 194, 276–286. [CrossRef]

49. Párez, I.; Pasandín, A.R. Moisture damage resistance of hot-mix asphalt made with recycled concrete aggregates and crumb rubber. J. Clean. Prod. 2017, 165, 405–414. [CrossRef]

50. Hardjito, D.; Wallah, S.E.; Sumajouw, D.M.J.; Rangan, B.V. Factors influencing the compressive strength of fly ash-based geopolymer concrete. Civ. Eng. Dimens. 2004, 6, 88–93.

51. Lloyd, N.A.; Rangan, B.V. Geopolymer Concrete with Fly Ash. In Proceedings of the Second International Conference on Sustainable Construction Materials and Technologies, Ancona, Italy, 28–30 June 2010.

52. Anuradha, R.; Sreevidya, V.; Venkatasubramani, R.; Rangan, B.V. Modified guidelines for geopolymer concrete mix design using Indian standard. Asian J. Civ. Eng. 2012, 13, 353–364.

53. Ferdous, M.W.; Kayali, O.; Khennane, A. A detailed procedure of mix design for fly ash based geopolymer concrete. In Proceedings of the Fourth Asia-Pacific Conference on FRP in Structure, Melbourne, Australia, 11–13 December 2013; pp. 11–13.

54. Junaid, M.T.; Kayali, O.; Khennane, A.; Black, J. A mix design procedure for low calcium alkali activated fly ash-based concretes. Constr. Build. Mater. 2015, 79, 301–310. [CrossRef]

55. IS:9103; Specification for Concrete Admixture. Bureau of Indian Standards (BIS): New Delhi, India, 1959.

56. IS:516; Indian Standard Methods for Tests for Strength of Concrete. Bureau of Indian Standards (BIS): New Delhi, India, 2006.