

Effect of Utilization of Agro-based Materials in Geopolymer – A Review

Pream Kumar S^{1}, A Chithambar Ganesh², Prem Kumar Vagestan³, Vijay Sankar. K⁴, Priyanka Murugesan⁵, and Sandip Baburao Chavan⁶*

¹Research Scholar, Department of Civil Engineering, Vel Tech Rangarajan Dr. Sagunthala R&D Institute of Science and Technology, Chennai, Tamil Nadu, India.

²Department of Civil Engineering, Vel Tech Rangarajan Dr. Sagunthala R&D Institute of Science and Technology, Chennai, Tamil Nadu, India.

³Faculty of Engineering and Technology, Villa College, QI Campus, Male, Maldives.

⁴Department of Civil Engineering, Sri Ranganathar Institute of Engineering and Technology, Coimbatore, Tamil Nadu, India.

⁵Department of Civil Engineering, Chennai Institute of Technology, Chennai, Tamil Nadu, India.

⁶Department of Civil Engineering, CSMSS Chhatrapati Shahu College of Engineering, Maharashtra, India.

Abstract. The global emission of greenhouse gases is largely attributable to the construction industry. One practical way to address environmental issues is to use waste resources in concrete. Farm manure is widely used in place of cement in the production of environmentally friendly concrete. Large quantities of Rice Husk Ash (RHA) are produced yearly, most of which is disposed of in landfills, severely degrading the environment. The usage of RHA as a precursor or alkaline binder in the synthesis of alkali-activated geopolymer, which is thought to be a workable way to lessen the serious issue and as well to prevent it. This new material is superior to conventional materials in terms of price and performance. This paper aims to outline an overview of the research on the application of geopolymer based on agro waste ash as a long-term, ecologically benign, and affordable building material. This study offers a thorough examination of the physio mechanical and workability characteristics of geopolymer concrete made of rice husk ash from agro-waste. The findings added to the body of evidence supporting the viability and sustainability of replacing conventional cement-based materials with geopolymer concrete that contains derivatives of agricultural waste as binding agents.

1 Introduction

Globally, a new degree of quickness has been attained. Infrastructure is one of the most important element that has shaped contemporary society. Beginning in caves, people used their creative and analytical minds to construct beautiful, durable houses. People still consider a nation's infrastructure to be its most valuable resource. Cement a widely used building

* Corresponding Author: preamkumars@sriet.ac.in

material all over the world. Nevertheless, their continued manufacturing and consumption harmed the environment. In PC manufacturing, anthropogenic CO₂ emissions made up between 5 and 8% of total emissions [1]. The increasing population and better infrastructure in both industrialized and developing countries are expected to contribute to this figure's growth. Apart from its adverse impact on the environment, PC has additional disadvantages that cast doubt on its sustainability, such as its excessive energy usage and dependence on non-renewable, naturally occurring raw resources. Manufacturing of cement causes a serious threat to the environment due to the release of carbon dioxide. Moreover, a higher temperature is required during the production. Such effects lead to global warming, thus bringing the earth closer to catastrophe. Despite this, cement is the primary binding material in the construction sector. Hence, there is an urge to look for a material equivalent to cement to protect the environment from the above causes. In order to overcome the above, secondary materials need to be introduced, which is supplement to the cementitious material. They emit less carbon dioxide than the national average. SCMs are leftovers and manufacturing waste from a variety of businesses. SCM's are need to be managed to protect the environment from pollution. The characteristics of OPC can be reflected by varying the quantities and combinations of SCMs. Fly ash, RHA, and corncob ash are a few types of supplementary cementitious materials. RHA is an agricultural waste and possess the application in biofuel [2]. SCM can be effectively utilized to produce concrete because it has a silica content of over 90%. RHA production was projected to have exceeded 70 million tons worldwide in the year 2016. RHA is increasingly harder to dispose of in rice-producing areas due to its massive quantity. Under controlled conditions, rice husk can be turned into ash, which can subsequently be used in building sectors. Researchers were drawn to RHA's possible use as a pozzolanic material by a number of features, which include pore structure, high silica, durability, reduced cost, and sustainability. Further, the use of RHA as supplementary material lowers CO₂ emissions. Numerous research has been examined how rice husk ash incorporation affects cement quantity reduction and compressive strength in concrete. Although adding RHA instead of cement improves concrete's CS, research indicates that the highest strength benefits come from a RHA to cement ratio of 10% to 30%. Strength improved at 15wt% replacement to cement as reported in the literature. Mahmud et al. [3] and Zhang et al. [4] reported 10wt% replacement also improved the strength over that of the control. Additionally, they discovered that CS was higher in concrete with a 15% RHA and that this reduction occurred at higher volumes. For all w/c ratios, 30% RHA has been considered the optimum percentage in replacement of cement. One possible explanation for the improved strength and durability using RHA is the fact that it has a low calcium hydroxide concentration, a small interfacial zone between matrix and aggregate, which results in reduced porosity. Because of the chemical reaction that happens among RHA and calcium hydroxide during hydration, RHA concrete that has more C-S-H gel added to it may have better qualities. Along with that, RHA mixed concrete that has controlled-incineration-generated CS has outstanding long-term performance.

GGBS (Ground Granulated Blast Furnace Slag) and FA (Fly ash) have been used as precursors in most works in geopolymer. These days, their usage in the production of cement is essentially limited to supplemental cementitious materials (SCMs). Presently, scholars are examining the suitability of alternative industrial residues, like RHA, which possess varied chemical and mineralogical compositions, as potential supplementary cementitious materials (SCMs). The term "rural residue" (RHA) describes the byproduct or agricultural leftover left over after milling rice. This material is usually not used to its full potential or disposed of in landfills, which has a detrimental impact as it poses serious pollution in the environment. The increased output of rice for humans leads to the generation of more RHA. Rice husk has not been used much in recent years, mainly for the purpose of generating steam in rice mills during the parboiling process. It is important to remember that RHA makes up about 25wt%

of rice husk. RHA can be used as a secondary raw material for cement. In the last 10 years, a notable improvement in using RHA has been noticed. The effectiveness of RHA as a pozzolan has been the subject of several studies and reviews, but not enough is known about how it affects the properties of fresh and hardened states. The present study reviews the properties of RHA and its production methods. Further, a detailed analysis was provided to the academic and construction sectors regarding the potential applications of RHA as precursors for alkali-activated materials in the industry.

1.1 Significance of the study

In recent studies, agro-based waste becomes significant material in the field of construction owing to its chemical composition, properties, and performance. Particularly, rice husk ash has been used either as a supplementary material or as alkaline binder in geopolymer due to the presence of high reactive silica. This study aims to provide a detailed review on properties of rice husk ash and its effect as a precursor and alkaline activator in geopolymer. Despite various research works having been carried out on rice husk ash as a pozzolanic material in geopolymer, lack of studies on its performance as an alkaline activator. In this regard, an objective and novelty of the present review is to critically analyse the properties and performance of agro-waste (rice husk) in geopolymer concrete as supplementary cementitious material and alkaline activator. This review provides detailed and thorough insights of rice husk ash, viz., material generation and performance in geopolymer. Moreover, this study provides a valuable insight into the use of agro-based waste materials in industrial communities for prospective use in building sectors.

2 Geo Polymer Concrete

2.1 Alumino-Silicate Material

The precursors used in the geopolymer concrete are derived from agricultural waste. An alkali-based binder initiates a chemical reaction – a polymerization which results in the formation of a robust and durable material. An essential step in the procedure is curing the mixture at a predetermined time and temperature. Byproducts like NaOH, KOH, Na₂SiO₃, or K₂SiO₃ are combined with metallic alkali. Because it creates less carbon dioxide, this material is beneficial for the environment even though it does not last as long as ordinary concrete.

Just two of the numerous excellent qualities of geopolymer materials are their resistance to corrosion and fire. Select the appropriate ingredients first. Next, create a slurry by mixing the metallic alkaline with the precursor. Pour the mixture into forms or molds after that. Lastly, let the concrete cure in a wet area. The curing of geopolymer varies from days to weeks to attain the target strength. After curing, the specimen is tested for strength to meet the standards. A consequence of the geopolymerization process is the amorphous alumino-silicate gel known as the geopolymer gel binder phase, which contains alkali. Nonreactive solid source material particles can be found at this step. Water is injected into the gel through its pore structure to mix the precursors. The structure of geopolymer differs from conventional ones, as it possesses C-S-H gel, where polymerization takes place in the geopolymer [5]. An alkaline solution influences the strength properties. In an extremely simple atmosphere, the process of hydrolysis—which enhances engineering qualities—is expedited. Permitting unrestricted movement of OH⁻ ions within the matrix may jeopardize and hinder the process. The significance of geopolymer concrete is presented in Figure 1.

2.2 Alkaline Activator

Alkaline activators such as potassium hydroxide, sodium hydroxide, potassium silicate, and sodium silicate are the most commonly used materials. The alkaline environment these alkali solutions create is essential for the dissolution of aluminosilicate minerals obtained from agricultural waste, which is why they are significant in the geopolymerization reaction. The geopolymer binder is created as a result of this dissolving process [6]. The composition of the aluminosilicate material affects how alkaline activators affect geopolymerization. While some changes in the characteristics of alkaline solutions may influence the final product, overall, these solutions have similar effects on the geopolymerization reaction. An aluminosilicate gel structure created through the chemical process called geopolymerization. An alkali metal affects the reaction rate and the final product. This inorganic polymer has an amorphous quality at high temperatures. Geopolymerization proceeds more quickly when heat is applied during the curing process than when it is done at room temperature. The alkalinity of the solution is influenced by NaOH and Na₂SiO₃, which affect geopolymerization. The solution has a higher alkalinity because sodium hydroxide is a stronger alkali than potassium hydroxide. Increased alkalinity can encourage higher degrees of geopolymerization, increasing the material's strength. Nonetheless, increased alkalinity can make a substance more fragile and prone to fracture. The predominant alkaline activator used in the geopolymer is sodium silicate (Na₂SiO₃) and sodium hydroxide (NaOH), which possess better properties.

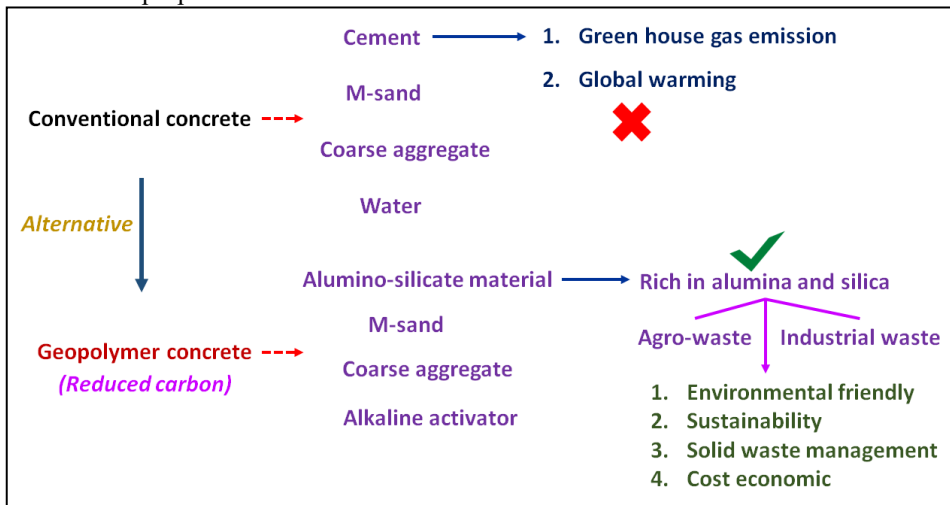


Fig. 1. Significance of geopolymer concrete over conventional

The performance of the geopolymer affected by various factors, viz., alkaline activator, liquid-binder ratio, curing method, temperature, and alkaline concentration. In the present study, the term 'binder' refers to the alumina-silicate precursor derived from agricultural waste. The term "alkaline solution" refers to NaOH and Na₂SiO₃ proportions. According to Palomo, the choice of alkaline liquid significantly influences the polymerisation process [7]. Reactions exhibit a significantly higher reaction when alkaline liquids, such as potassium/sodium silicate, are used than when hydroxide is used. In addition, a study on the geopolymerization revealed that the NaOH solution, compared to the KOH solution, possesses higher mineral dissolution.

In cement concrete, the hydration process takes place, whereas in geopolymer, a polymerization takes place in which alumino-silicate material reacts with alkaline activator, thus forming a three-dimensional polymeric network. The stages of polymerization include

(i) dissolution of precursors into alkaline activator, (ii) polycondensation to form Si-O-Al-O bonds, and (iii) formation of a three-dimensional rigid structure (N-A-S-H). Compared to conventional cement concrete, geopolymer possesses better properties and enhanced performance suited for varied building applications.

3 Agro-based Waste Materials

3.1 Properties of Agro-based Materials

Significant levels of lignin, cellulose, hemicellulose, and moisture are present in rice husks. Several factors, viz., variety, location, climate, soil, fertilizer, etc., affect the quality of rice husks. They are less suitable for some applications because of their higher ash content when compared to other waste products made of silica [8]. The ash content of RHA can be reduced by as much as 92% with the use of sodium hydroxide (NaOH). Additionally, this procedure eliminates silica and produces sodium silicate. Acid solutions enhance the surface area and pozzolanic properties of rice husks, while also eliminating metallic contaminants by leaching. Residual ash from rice husk, known as RHA characterized by its X-ray amorphous nature, ultrafine particle size, and high porosity. Before being utilized as precursors of solid-composites (SCMs), it is necessary to conduct an inquiry of the physical features of the material which is essential. Milling can reduce particle size and enhance surface area, but it does not exert a substantial impact on the chemical composition. Maximizing the characteristics of RHA is essential for its application in Advanced Materials (AAMs).

A sustainable binder is required to address the necessity of decreasing emissions from cement production and non-renewable natural resources. Reactive high-alumina (RHA) based alkali-activated materials (AAMs) exhibit enhanced mechanical and durability properties compared to polycarboxylate (PC) as a binder [9]. These characteristics depend on the kind of activator that is employed, the circumstances in which the material is cured, and the degree to which RHA is substituted for other components.

3.2 Effect of industrial waste and its significance

An alternative to conventional geopolymer uses industrial waste material, viz., slag, fly-ash as a binding material. Particle size of alccofine plays a major role in physio-mechanical properties, viz., density, compression, and tensile strength of geopolymer owing to its ultra-fine particles, which fill the voids in the matrix. In the study, alccofine is used as a supplementary material in geopolymer by incorporating with GGBS and fly-ash, and studied the properties of workability and mechanical. Alccofine in geopolymer potentially enhanced the performance of the concrete as evaluated by experimental methods [10].

Utilization of alccofine in geopolymer promotes the polymerization and as well fills the voids. It also enhanced the durability of concrete by resisting chloride penetration and acid attack. Alccofine in the presence of calcined treated clay and concentrated NaOH yields higher strength at ambient temperature. Hence, alccofine in geopolymer enhances the strength and durability. Previous studies reported that incorporation of alccofine in geopolymer improved the fresh and hardened properties, particularly when alccofine and fly-ash were mixed at varied ratio resulted in better mechanical properties, viz., compression, tensile, and flexural strength [11,12]. The microstructural analysis showed that the addition

of alccofine led to a reduced porosity due to a denser microstructure, which enhances the mechanical properties of the geopolymer concrete.

3.3 Properties of Rice Husk Ash (RHA)

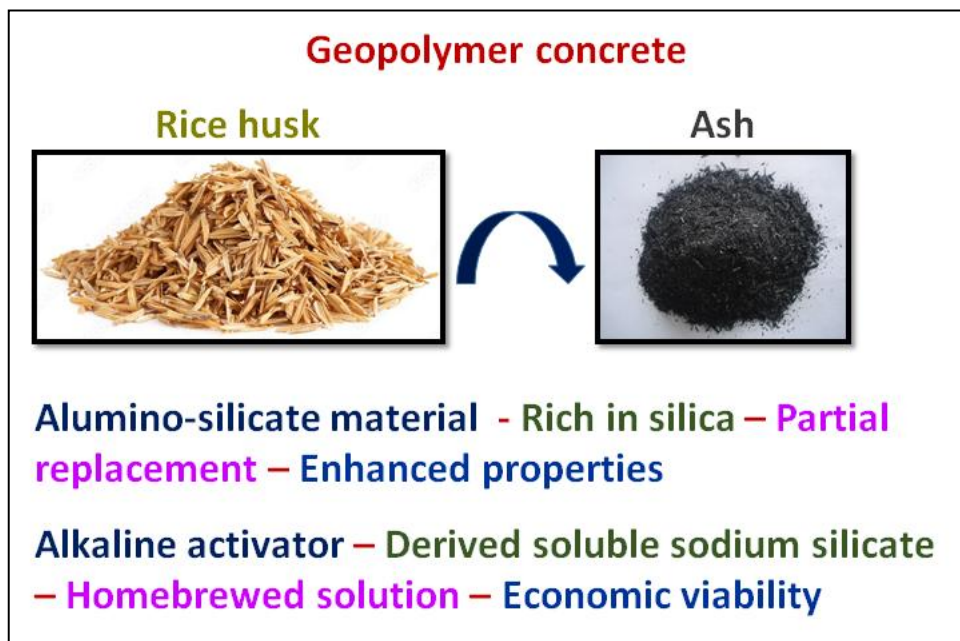


Fig. 2. Effect of rice husk ash (agro-based material) in geopolymer

About 50% of people on the planet eat rice, which is an essential food staple. They are growing in large quantities all over the world, including China, India, Indonesia, and other countries. One such waste is rice husk producing in large quantities in many of the world's rice-producing nations is rice husk. A skin covers the grain in rice husk, which is separated after milling. Rice husk is the name given to the tough outer coat that covers paddy grain. During milling, rice husk is removed from the seed. The milling process results in the production of lignocellulosic materials; for example, 1 ton of rice husk can be obtained from 5 tons of rice paddy. The annual production of rice husk is projected to be 120 million tons. Because of the large amount of rice husk produced, it is required to repurpose it for the production of bioethanol and as a fuel source for enterprise heat generation. In accordance with the European Union's waste management legislation, replacing coal in industries with rice husk as fuel can lower carbon emissions from burning coal and promote environmental preservation [13]. RHA is a byproduct after burning in a boiler, which accounts for 20–25% of the weight. Pre-treatment, burning, milling, and separation are the steps involved in ash production. Its composition is directly influenced by the method of combustion, which is usually either uncontrolled open burning or controlled incineration. Ash that is produced by uncontrolled open combustion has a much higher rate of crystallization and has insufficient pozzolanic properties that are insufficient. The presence of silica in ash under uncontrolled burning is inert. Moreover, non-reactive silica such as tridymite and cristobalite in RHA was produced under uncontrolled combustion. The majority of their hue is dark, which is related to the high carbon content. Rice husk ash derived from rice husk under controlled conditions of burning improves the pozzolanic activity and increases the amorphous silica by reducing the crystalline phase. Figure 2 illustrates the functions of rice husk ash in geopolymer.

Moreover, utilization of RHA reduces the environmental issues/pollution owing to the controlled burning. Previous studies reported various methods to produce rice husk ash under different temperatures. The composition of elements such as carbon, silica, and LOI in RHA is influenced by temperature, length, and time. The physical characteristics of RHA are likewise influenced by these variables. It has been reported that silica in RHA changes into a crystalline condition when the temperature is raised above 900°C for a period. Moreover, amorphous silica can become crystalline when heated to a temperature of 700°C for a sustained period. Large amounts of crystalline silica were formed when subjected to temperatures higher than 1150°C [14]. The pozzolanic characteristics of RHA may be affected, and the specific surface area may decrease if certain impurities are not removed. Milling is one of the critical stages in the production. RHA obtained after milling undergoes various factors, such as the type and size of gradation, which depend on grinding techniques. Smaller particles of RHA enhance the surface area and thus increase the pozzolanic activity of the material [15].

4 Conclusion

Geopolymer is one such material alternative to Portland cement with enhanced properties. In the present study, a geopolymer incorporated with rice husk ash has been studied, and its properties, such as physico-mechanical and durability, have been studied. Compared to conventional concrete, rice husk ash-based geopolymer showed better properties. Waste-derived secondary material were getting attention in the building sectors due to economic feasibility. However, a serious concern arises while using waste-derived materials in geopolymer, addressing the reaction and performance. RHA incorporated geopolymer possesses a denser microstructure with a more condensed structure than conventional concrete. The porosity and pore diameter are more refined and smaller. RHA possesses better mechanical properties and is durable in nature. The presence of minerals in RHA, such as gehlenite, feldspathoids, and zeolite, greatly influences the strength. Addition of alccofine with RHA and GGBS makes the new application on waste materials, rather than a combination with fly-ash and metakaolin. From the observation, a combination of fly-ash, GGBS, and alccofine at a percentage of 50%, 35%, and 15%, respectively, showed better results in strength and durability. In addition, optimization of activators and raw materials could also influence the strength. Thus, RHA and alccofine in geopolymer concrete potentially enhance the strength more than that of conventional concrete. This review addressed the waste management and the methods to reduce the carbon footprint.

References

1. M.C.G. Juenger, F. Winnefeld, J.L. Provis, J.H. Ideker, Advances in alternative cementitious binders, *Cem. Concr. Res.* **41** 1232–1243 (2011). <https://doi.org/10.1016/j.cemconres.2010.11.012>.
2. M.A. Khan, A. Zafar, A. Akbar, M.F. Javed, A. Mosavi, Application of gene expression programming (GEP) for the prediction of compressive strength of geopolymer concrete, *Materials (Basel)*. **14** 1106 (2021). <https://doi.org/10.3390/ma14051106>
3. H. Bin Mahmud, M.F.A. Malik, R.A. Kahar, M.F.M. Zain, S.N. Raman, Mechanical properties and durability of normal and water reduced high strength grade 60 concrete containing rice husk ash, *J. Adv. Concr. Technol.* **7** 21–30. (2009). <https://doi.org/10.3151/jact.7.21>

4. A. El-Dakrouy, M.S. Gasser, Rice husk ash (RHA) as cement admixture for immobilization of liquid radioactive waste at different temperatures, *J. Nucl. Mater.* **381** 271–277 (2008). <https://doi.org/10.1016/j.jnucmat.2008.08.026>
5. C.K. Lau, M.R. Rowles, G.N. Parnham, T. Htut, T.S. Ng, Investigation of geopolymers containing fly ash and ground-granulated blast-furnace slag blended by amorphous ratios, *Constr. Build. Mater.* **222** 731–737 (2019). <https://doi.org/10.1016/j.conbuildmat.2019.06.198>
6. M.S. Meddah, T.R. Praveenkumar, M.M. Vijayalakshmi, S. Manigandan, R. Arunachalam, Mechanical and microstructural characterization of rice husk ash and Al₂O₃ nanoparticles modified cement concrete, *Constr. Build. Mater.* **255** 119358 (2020). <https://doi.org/10.1016/j.conbuildmat.2020.119358>
7. A. Fernández-Jiménez, A. Palomo, Composition and microstructure of alkali activated fly ash binder: Effect of the activator, *Cem. Concr. Res.* **35** 1984–1992 (2005). <https://doi.org/10.1016/j.cemconres.2005.03.003>
8. A.-V. Lăzărescu, H. Szilagyi, C. Baeră, A. Hegyi, Parametric studies regarding the development of alkali-activated fly ash-based geopolymer concrete using Romanian local raw materials, in: *Proceedings, MDPI*, 2020: **11**. <https://doi.org/10.3390/proceedings2020063011>
9. N.M. Azad, S.M.S.M.K. Samarakoon, Utilization of industrial by-products/waste to manufacture geopolymer cement/concrete, *Sustainability.* **13**, 873 (2021). <https://doi.org/10.3390/su13020873>
10. L. Nishanth, N.N. Patil, N. Kumbar, S. Kaveti, D. Kar, Influence of E-Coli on workability and strength characteristics of self-consolidating geopolymer concrete based on GGBFS, flyash and alccofine, *Mater. Today Proc.* **80** 369–376 (2023). <https://doi.org/10.1016/j.matpr.2022.10.183>
11. P. Goyal, P. Bathinda, R.K. Singla, P. Kaur, Experimental study: Alccofine as strength enhancer for geopolymer concrete, *Int. J. Adv. Res. Ideas Innov. Technol.* **5**, 227–231 (2019).
12. S.K. Saxena, M. Kumar, N.B. Singh, Effect of Alccofine powder on the properties of Pond fly ash based Geopolymer mortar under different conditions, *Environ. Technol. Innov.* **9**, 232–242 (2018). <https://doi.org/10.1016/J.ETI.2017.12.010>.
13. M. Soutsos, A.P. Boyle, R. Vinai, A. Hadjierakleous, S.J. Barnett, Factors influencing the compressive strength of fly ash based geopolymers, *Constr. Build. Mater.* **110**, 355–368 (2016). <https://doi.org/10.1016/j.conbuildmat.2015.11.045>
14. A. Muthadhi, S. Kothandaraman, Optimum production conditions for reactive rice husk ash, *Mater. Struct.* **43**, 1303–1315 (2010). <https://doi.org/10.1617/s11527-010-9581-0>
15. P. Nath, P.K. Sarker, Effect of GGBFS on setting, workability and early strength properties of fly ash geopolymer concrete cured in ambient condition, *Constr. Build. Mater.* **66**, 163–171 (2014). <https://doi.org/10.1016/j.conbuildmat.2014.05.080>.