engineering proceedings

MDPI

Proceeding Paper

A Review on the Effect of Fly Ash, RHA and Slag on the Synthesizing of Coal Bottom Ash (CBA) Based Geopolymer †

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† Presented at the 2nd International Electronic Conference on Applied Sciences, 15–31 October 2021.

Abstract: Geopolymerization is widely used in the construction sector for its characteristics of strong compressive strengths, quick hardening, long-term durability, fire resistance, and erosion resistance. This paper has gone through the geopolymer performances utilizing coal bottom ash (CBA), CBA blended with fly ash (FA), CBA mixed together with slag, and CBA with rice husk ash (RHA). CBA shows a better performance than FA in the compressive strength. This paper has discovered several elements that influence geopolymerization, the curing time, the curing temperature, the silicate and hydroxide ratio, and grinding CBA surfaces. The combination of CBA and RHA is suitable for lightweight concrete, as the range of the volumetric weight is within 1192 kg/m^3 to 1655 kg/m^3. The slump result decreases, as the ratio of CBA and slag increases. Slag particles are uneven in shape, which increases water consumption and leads to a honeycombed structure, whereas CBA particles are spherical in shape, which enhances workability.

Keywords: geopolymer; CBA-based geopolymer; slag; rice husk ash; fly ash; water glass solution (WGS)

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Citation: Gulam, N.F.B.A.; Kaish, A.B.M.A.; Mahmood, A.; Raman, S.N.; Jamil, M.; Hamid, R. A Review on the Effect of Fly Ash, RHA and Slag on the Synthesizing of Coal Bottom Ash (CBA) Based Geopolymer. *Eng. Proc.* **2021**, *11*, 20. https://doi.org/10.3390/ASEC2021-11164

Academic Editor: Samuel B. Adeloju

Published: 15 October 2021

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1. Introduction

Geopolymer concrete is a type of concrete that is made by reacting materials containing aluminates and silicates with a caustic alkali activator. Waste materials such as coal ash or slag from iron and metal production are often used to help achieve a cleaner environment. This is because the waste is actually encapsulated in concrete and does not have to be disposed of during use. Geopolymer concrete does not require heating to be manufactured and does not produce carbon dioxide. The standard Portland cement-based concrete or Ordinary Portland Cement (OPC) requires heat and carbon dioxide. There are nine different types of geopolymer, but the largest potential application category for transportation infrastructure is made up of aluminosilicates materials and can be used to completely replace Portland cement in concrete buildings [1]. These geopolymers are based on thermally activated natural materials or industrial by-products (coal bottom ash (CBA), fly ash (FA), or slag) to provide with sources of silicon (Si) and aluminum (Al), which are dissolved in an alkaline activation solution, and the polymer chains and networks are then polymerized to form a hardened binder. This system is commonly referred to as alkali-activated cement or inorganic polymer cement [1].

In recent years, people's awareness of the quantity and diversity of hazardous solid waste and its impact on human health has continued to increase. Increasing attention to the

environmental consequences of waste treatment has led to investigations into new ways of using it. The biggest problem facing the industry is the safe and efficient disposal of by-products such as emissions, sludge, and a large amount of coal ash generated during the combustion of coal for power generation. It is estimated that the amount of FA produced will be about 780 million tonnes annually. While the US Environmental Protection Agency and EPA have reported that, it estimated that 140 million tons of coal ash are produced annually. This makes coal ash the second largest industrial waste stream in the United States, after mining waste [2].

2. Chemical Composition of CBA

In keeping similarity with [3], among the analyzed chemical composition of the CBA, the highest percentage is 29.15% silica (SiO_2), followed by 26.685% alumina (Al_2O_3). Therefore, there may be a slightly lower sulphur trioxide (SO_3) content in the bottom ash. This may be due to the low porosity of the bottom ash particles [4], which makes the CBA classified in the F-class based on the ASTM C 61803. Due to the different sources of coal used, there are slightly differences in the chemical composition of the CBA. This classification is strengthened by [5], where the total percentage of SiO_2, Al_2O_3, and Fe_2O_3 in the CBA is more than 70%. The following Table 1 is the chemical compositions of CBA in different power plants.

Table 1. Chemical compositions of the coal bottom ash (CBA) in different power plants.

Power Plant Station/Chemical Composition (%)	Spanish Power Plant	TNB Electric Power Plant, Perak, Malaysia	Tanjung Bin Power Station, Johor, Malaysia	Guru Hargobind Power Plant Bathinda, India	Seocheon Coal-Fired Power Plant, South Korea
SiO_2	52.30	54.80	29.15	56.44	44.2
Al_2O_3	25.14	28.50	26.68	29.24	31.5
Fe_2O_3	9.23	8.49	7.28	8.44	8.9
CaO	2.37	4.20	16.36	0.75	2.0
MgO	1.84	0.35	1.51	0.40	2.6
Na_2O	0.66	0.08	1.15	0.09	-
K_2O	3.72	0.45	0.53	1.29	-
TiO_2	1.45	2.71	-	3.36	2.4

3. Performance Comparison of CBA with Other Pozzolans

3.1. Performance of the CBA Geopolymer

According to [6], it has been stated that the average compressive strengths for pure CBA geopolymer paste was 13.58 MPa, 18.34 MPa, 24.06 MPa, and 22.77 MPa after the pastes were cured at 70 °C and tested after 3, 7, 14, and 28 days. The geopolymer paste reached its maximum compressive strength after 14 days, according to general observations; these findings also indicated that as the curing period lengthens, mortar strength increases [7]. At an elevated temperature, the microstructure of CBA appears to be weakened after 14 days [8]. However, the gap in the compressive strengths between the 14th and 28th days is not statistically significant. In order to check the quality of the geopolymer in a different temperature, 100% CBA specimens were mixed, prepared separately and were cured until 5th, 10th, 15th, and 25th days. The compressive strengths after these days were recorded as shown in Figure 1 and the highest strength was found to be 6.95 MPa. This means that the curing temperature has a significant impact on the strength of the geopolymer concrete. Another important idea claims that increasing the concentration of alkali contained in Na and K metallic ions or decreasing the silicate SiO_2 concentration increases the compressive strength. Singh and Bhardwaj [9] determines that increasing the ratio of sodium silicate to sodium hydroxide has an impact on the geopolymer com-

pressive strength performance. The compressive strength increases, as the Si/Al ratio increases with the increasing percentage of NaOH. Furthermore, the use of finer CBA (4.3 mm) increased the compressive strength due to the inherent pore refinement action of finer particles filling the pores in the paste, increasing hydration products formed during pozzolanic reactions [10]. Physically and chemically, ground CBA resembles FA. Almost all investigations have revealed that adding grinded CBA reduces the compressive strength at early ages. It was discovered that replacing cement with bottom ash had a poor initial curing performance. The performance of the combinations continued to improve even at the age of seven days. When the curing time was increased to 28 days, the performance of the combinations improved dramatically. All of the cement mixtures' compressive strength values are higher than the control sample. Due to the natural pore refinement activity, finer particles filled the pores in the paste, increasing hydration products generated during pozzolanic reactions, and the incorporation of finer CBA with a size of 4.3 mm showed an improvement in the compressive strength. Previous researcher [10,11] has found that the by reducing the particle size of CBA in concrete, the qualities of the concrete are enhanced. The compressive strength of CBA is influenced by the grinding time of CBA with a highball mill. Most research recommended that, the grinded CBA has a potential to be a good pozzolanic material by the increase in fineness. Figure 2 below shows the SEM picture of the 24 h ground bottom ash paste. The particles are closely connected together in the left image of Figure 2. The geopolymer matrix generated by the dissolving of bottom ash and a mixing of sodium hydroxide and sodium silicate solution interlinks the bottom ash particles and the sand particles. The failure zone is depicted in the right image of Figure 2. The bottom ash particles, which are not dissolved in the geopolymer matrix, seem to be split from the gel itself in the failure zone.

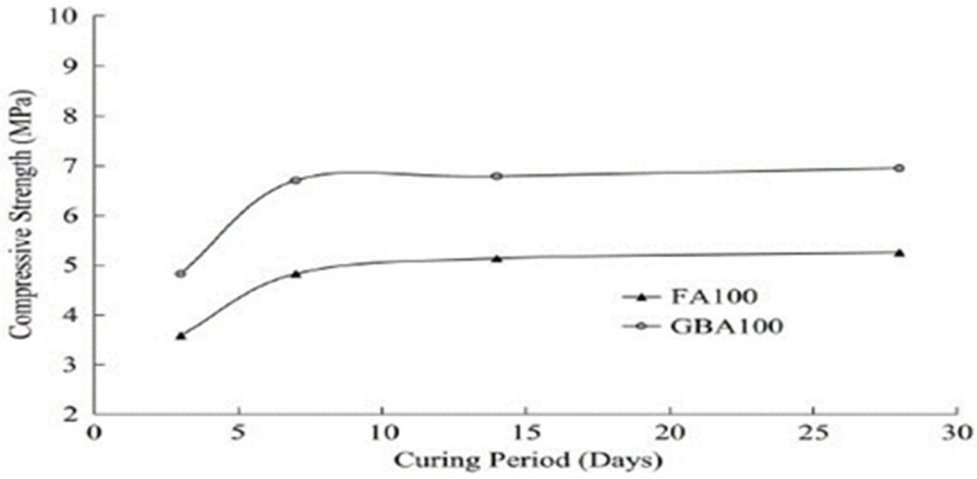

Figure 1. Compressive strengths of geopolymer paste samples made "separately" using 100 percent fly ash (FA) and 100 percent of ground bottom ash to study the effects of the room-temperature curing.

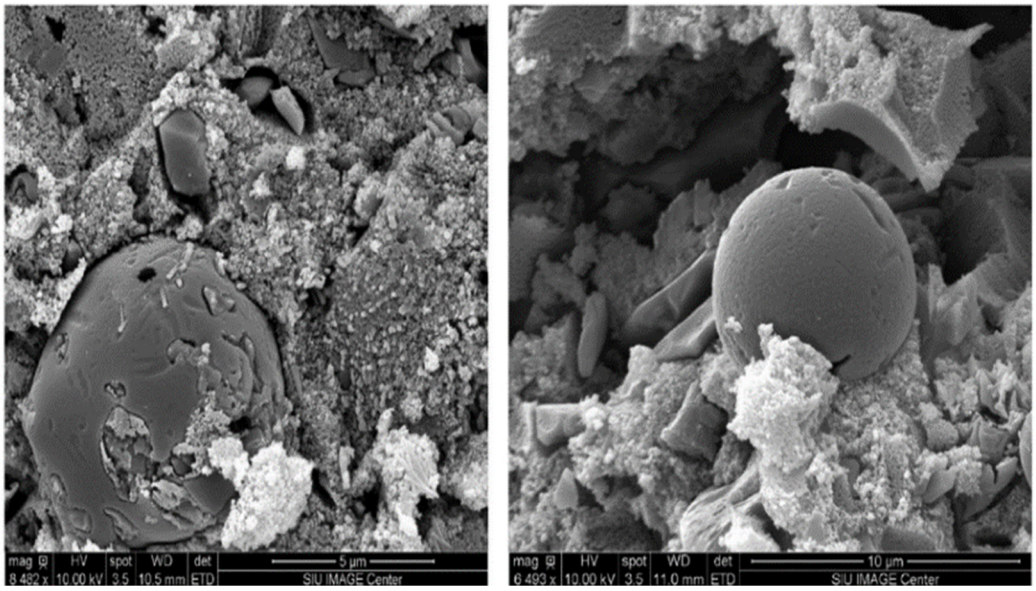

Figure 2. Figure left side: The particles are closely connected together. While, Figure right side: The bottom ash particles, which are not dissolved in the geopolymer matrix, seem to be split from the gel itself in the failure zone.

3.2. Performance of the CBA and Rice Husk Ash (RHA) Geopolymer

As mentioned before, geopolymer is an inorganic polymer material made up of alumino-silicate networks, which are developed when alumino-silicate materials react in a high alkaline environment., which is the result of reactions between alumino-silicate materials in a high alkaline condition. Coal bottom ash (CBA) and rice husk ash (RHA) are combined, with the CBA serving as the principal source of reactive alumina and silicate and the RHA serving as the key source of reactive silica.

According to Van Phuc & Thang [12], geopolymers with an average compressive strength of 17.4 MPa after 28 days, a water absorption of 259.9 kg/m^3, and a volumetric weight of 1655 kg/m^3 were produced using a solid powder mix of 50% CBA and 50% RHA and alkaline activated with 28% (by weight of solids) of water glass (silica modulus of 2.5). After a period of time, with the same portion of solid powder mix as in Van Phuc & Thang [12] with alkaline activated by using the concentration of sodium silicate to 30%, after an average of 28 days, the compressive strength of CBA with RHA was determined to be 37.41 MPa, with a water absorption of 129.94 kg/m^3 and a volumetric weight of 1192 kg/m^3 [13]. Following the same procedure, with 35% CBA, 35% of RHA, and 30% of a water glass solution, it achieved the best performance where the compressive strength was 17.41 MPa, the volumetric weight was 1485.30 kg/m^3, and the water absorption reached 189.94 kg/m^3 [14]. These results from three different papers were in good compliance with the ASTM C55 and C90 requirements for the development of lightweight concrete. The SEM images of coal bottom ash and the blended rice husk ash can be seen in the Figure 3. The summary of the specimens performances can be shown in the Table 2.

Table 2. Engineering properties of the geopolymer (CBA + rice husk ash (RHA)).

Mixture Proportions	Volumetric Weight (kg/m^3)	Water Absorption (kg/m^3)	Compressive Strength (MPa)
50% CBA + 50% RHA 28% sodium silicate	1655	259.9	17.4
50% CBA + 50% RHA 30% sodium silicate	1192	129.94	37.41
35% CBA + 35% RHA 30% sodium silicate	1485.30	189.94	17.41

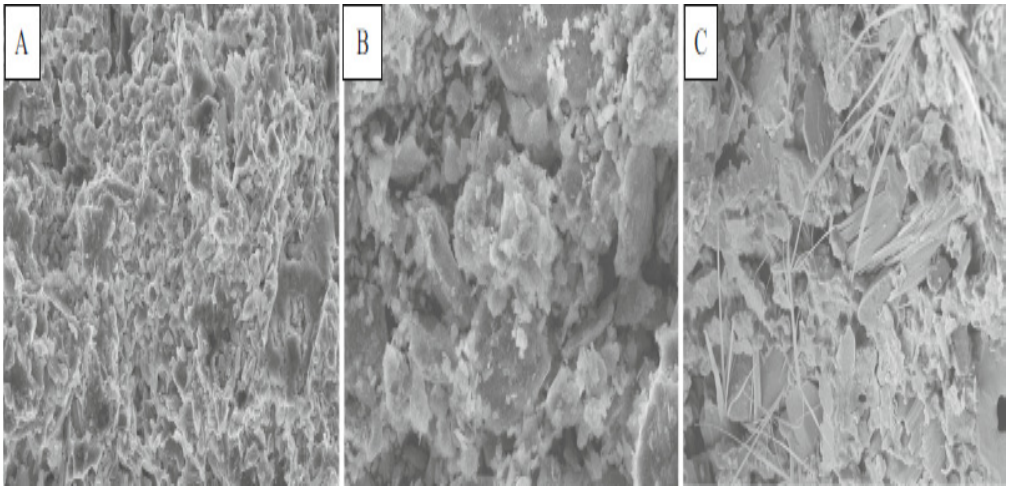

Figure 3. SEM image of RHA, (**A**) coal bottom ash, (**B**) and geopolymer with mixture proportions 35% of coal bottom ash, (**C**) 35% of rice husk ash with 30% of sodium silicate, as can be seen that appearance of a new phase with many long and thin rods [as shown in Figure 3C] as this morphology did not appear in any of the raw materials in image A and B.

3.3. Performance of the CBA and FA Geopolymer

Apart from that, the combination of CBA and coal FA as the geopolymer paste shows very satisfied performances in terms of the compressive strength. According to [15], the 90% of CBA and 10% of coal FA (CBA90FA10) combination generated the highest compressive strength among all the coal fly ash and ground bottom ash combinations, i.e., 22.44 MPa after 14 days, while the compressive strength of the combination of 50% of CBA and 50% of coal FA (CBA50FA50) was found to be 20.82 MPa after 14 days of the curing period. On the other hand, the geopolymer with 70% of CBA and 30% of coal FA (CBA70FA30) recorded, after 14 days of the curing period, the compressive strength achieved to be around 22.13 MPa. The results revealed that as the curing period is lengthened, the strength increases. In addition, the curing temperature has a significant impact on the strength of geopolymer concrete. The compressive strength appears to decrease after 14 days in many situations. Nevertheless, the difference of the compressive strengths between 14 and 28 days may not be statistically significant. Besides that, as the ratio of sodium silicate to sodium hydroxide increases, the compressive strength increases. This increasing pattern of compressive strength is due to the excess sodium silicate hinders water evaporation and the structure formation. From [16], 10M of NaOH concentration is suitable for both raw materials. It can also be seen that during the curing times of 14 and 28 days, even if the proportion is increased, no significant increase in the compressive strength of the paste is recorded. This theory supported by Paija et.al [6], which has found that the CFA/CBA ratio and the concentration of the activating solution may have a considerable impact on the mechanical characteristics of geopolymer made from FA and bottom ashes. The following Table 3 is the engineering properties of the geopolymer (CBA + FA) specimens.

Table 3. Engineering properties of the geopolymer (CBA + FA) specimens.

Mixture Proportions	Compressive Strength at the Room-Temperature Curing	Compressive Strength (after 14th Days at the Elevated-Temperature Curing)
50% CBA + 50% FA	-	20.82 MPa
70% CBA + 30% FA	-	22.13 MPa
100% CBA	6.95 MPa	24.06 MPa
100% FA	5.25 MPa	20.46 MPa

3.4. Performance of the CBA and Slag Geopolymer

The engineering characteristics of concrete including CBA and granulated blast furnace slag have been studied. It was discovered that when the mix proportion of granulated blast furnace slag + coal bottom ash increases, the workability of new concrete decreases. This might be related to the particle form of the substance, according to [17]. CBA particles are spherical in shape, which improves workability, whereas slag particles are irregular in shape, which increases water consumption and leads to a honeycombed structure, which may impact workability performance, and aggregate porosity may also influence workability. Although the water content in the mixture was increased, the workability of the mortar decreased when 75% of bottom ash was combined with it. This was related to the angular form and irregular texture of bottom ash impacting high-interparticle friction [18]. Concrete's water absorption capacity is influenced by its permeability and porosity. Because the replacement components have a higher water absorption capacity than sand, concrete permeability is important. Porosity is vital for the concrete's surface [19]. The GBFS and CBA particles have a distinct surface texture than sand. The creation of a stronger connection between the aggregates and the cement paste is aided by a rougher texture. As a result, the potential replacement of granulated blast furnace slag combined with coal bottom ash for the concrete geopolymer development should be in a less ratio, or new precautions to lessen water absorption capacity should be considered. Second, replacing CBA and slag as fine particles in concrete reduces the compressive strength, due to the fact that the blend of CBA+ slag +FA is higher in compressive strength than the combination of CBA + slag [20]. It is mentioned that the existence of FA in the mixture exerts a balancing effect to some extent as can be seen in Table 4 below, the last proportions contained fly ash (FA) has significantly affecting the strength of the specimens. It is previously been reported that FA contributes to the compressive strength and improves the durability of the concrete. The compressive strength of the concrete is determined by the curing time and temperature, since as the curing time and temperature increase, the compressive strength increases.

Table 4. Engineering properties of the geopolymer CBA with granulated blast furnace slag (GBFS) specimens.

Mixture Proportions	Measured Slump (cm)	Water Absorption (%)	Compressive Strength after the 7th Day (MPa)	Compressive Strength after the 28th Day (MPa)
100% Slag cement 100% aggregates	14	4.14	24.25	37.77
100% slag cement 30% GFBS + 30% CBA	6	6.87	14.14	21.91
100% slag cement 15% GFBS + 15% CBA	10	6.11	17.34	27.54
100% slag cement 25% GFBS + 25% CBA	6	6.66	15.63	25.67
95% slag cement + 5% FA 5% GFBS 5% + 5% CBA	13	4.4	21.30	33.22

4. Conclusions

The conclusions that can be drawn throughout this study are there are several factors affecting the development of geopolymers. The CBA geopolymer and the CBA + FA geopolymer investigation has found that the curing period lengthens, the mortar strength increases and the increase in strength for curing periods beyond the 14th day is not very significant. Because prolonged curing at elevated temperatures breaks the granular structure of the geopolymer mixture, the compressive strength decreases at higher temperatures for longer periods of time. Secondly, the curing temperature is found to be a vital factor in geopolymerization as explained in Section 3.1. Thirdly, increasing the concentration of alkali contained in Na and K metallic ions or decreasing silicate SiO_2 increases the

compressive strength. This is because excess sodium silicate hinders water evaporation and structure formation. The matrix activated with potassium silicate KOH obtains the greatest compressive strength, while sodium silicate/NaOH-activated matrixes are generally weaker followed by potassium silicate.

Author Contributions: Conceptualization, N.F.B.A.G. and A.B.M.A.K.; methodology, N.F.B.A.G.; validation, M.J. and A.B.M.A.K.; formal analysis, N.F.B.A.G. and A.B.M.A.K.; investigation, N.F.B.A.G., R.H. and A.B.M.A.K.; resources, S.N.R. and M.J.; data curation, N.F.B.A.G. and A.B.M.A.K.; writing—original draft preparation, N.F.B.A.G.; writing—review and editing, N.F.B.A.G., A.M. and A.B.M.A.K.; visualization, A.B.M.A.K.; supervision, R.H., M.J., S.N.R. and A.B.M.A.K.; project administration, M.J. and A.B.M.A.K.; funding acquisition, S.N.R., M.J., R.H. and A.B.M.A.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research is funded by the Ministry of higher Education, Malaysia through the Fundamental Research Grant Scheme (FRGS/1/2019/TK01/UKM/02/2).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge Universiti Kebangsaan Malaysia and Ministry of higher Education, Malaysia for providing the necessary opportunities and funding through "Research Graduate Assistance" scheme under the project number FRGS/1/2019/TK01/UKM/02/2.

Conflicts of Interest: The authors declare that there is no conflict of interest.

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