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DEVELOPMENT OF HYBRID GEOPOLYMER CONCRETES FROM BINARY AND TERNARY BLENDS OF ALUMINA-SILICATE SOURCE MATERIALS

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ABSTRACT

Hybrid geopolymer concretes were developed from alkaline activated blends of silicate-source materials in binary/ternary combinations. Portland cement concrete items were cured in water while the geopolymer concrete products were cured in drying kiln maintained at an average temperature of 70 degrees Celsius, strength assessments were conducted on cubes and laboratory beam samples. Results show that kaolin and rice husk ash geopolymer concretes had strengths lower than the strength of Portland cement concrete, the hybrids had similar strengths patterns as Portland cement concrete except for binary blends of fly ash and rice husk ash which resulted in 21 and 12 percent higher compressive and flexural tensile strengths respectively at 28 days. Primary and hybrid geopolymer concretes have been captured on a pattern of strength development described by the silica/alumina ratio, so that desirable geopolymer concrete properties can be obtained by adjusting the proportions in the blends of silicate source materials.

1. INTRODUCTION

Being the second most-consumed resource after potable water at an average of 3.5 billion tonnes per annum (Mehta, 2002; Czigler *et al.,* 2020) Portland Cement production constitute 7 percent of the total anthropogenic gasses released into the atmosphere (Mehta, 2001; Brogan, 2021), and is responsible for about 85 percent of the total carbon dioxide emissions caused by concrete at 250 kg CO_2/m^3 (Jotangia and Batikha, 2021), calcination accounts approximately for two-thirds of the total greenhouse gas emissions related to cement production (Czigler *et al.,* 2020). Jotangia and Batikha (2021) have suggested that Geopolymer cement could be a novel cement approach to decarbonisation pathways for the cement industry which may replace maximum of 5 and 10 percent of the existing cement by 2030 and 2050 respectively (Obrist, 2020; Favier *et al*., 2018), at which time the main source of Portland cement may be in short supply (Adeola 2019). The development of geopolymer materials (Davidovits, 1994) has led to enormous research efforts in prospecting rich alumina-silica waste materials as source materials for producing Geopolymer concrete (Vijaya Prasad and Arumairaj, 2019). These new cements/binders produce geopolymer concrete characterised by high mechanical performance, low energy cost and low pollutant gas emission and environmental impact (Fernandez-Jiminez, 2003; Nawaz et al 2020). The successes of producing geopolymer concretes from the utilization of recycled wastes such as fly ash, blast furnace slag, phosphogypsum, recycled aggregates, red mud, kraft pulp production residue, agricultural waste ash, etc., as construction materials (Safiuddin *et al*., 2010) show encouraging prospects. Geopolymer and Portland cement concrete technologies have been demonstrated (Tempest *et al,* 2015) to have broad similarity for mixing, placing, component design, appearance, and long-term performance, such that the gradual adoption of the material would seem more familiar than disruptive, and its utilisation has been projected to have a 7 percent probability globally (Assi *et al*., 2020). Among potential applications, *g*eopolymer concrete has been found to also be adequate for repair of tunnel-lining structures (Chen *et al,* 2019). However, studies investigating suitable combinations of multiple alumina-silicate bearing materials in determining optimal performance characteristics of hybrids geopolymer concretes are still limited.

1.1 Chemistry of Geopolymer Concrete

Conceptually, the formation of geopolymers is quite simple. Geopolymer cements are high-alkali (Potassium/Sodium)-Poly-(sialate-siloxo) chemical compounds, resulting from an inorganic poly-condensation reaction, termed as geo-polymerization yielding three dimensional zeolitic frameworks or polymeric chain and ring structure consisting of Si-O-Al-O bonds (Davidovits 1994), taking one of three basic forms depending on the ratio of silicon to aluminium (Xu and Van-Deventer, 2000). The products formed may be amorphous or semi-crystalline in structure depending on the temperature of geopolymerization. The exact mechanism of setting and hardening of the geopolymer material (as a binder), and also its reaction kinetics are not clear (Hardjito, 2005). However, the most proposed mechanisms (Xu and Van-Deventer 2000; Davidovits *et al.*, 1999; Mehta and Siddique, 2018) consist of dissolution of silicon and aluminium atoms from the source material from the action of hydroxide ions, transportation, and orientation, condensation of precursor ions into monomers, and setting or polycondensation/polymerization of monomers into polymeric structures. Concentrated activators are needed also dissolve calcium-rich solutions (Suresh Kumar *et al.*, 2020), otherwise, geopolymerization may cease at later ages when the activators are used up in dissolving the calcium at earlier ages (Zhang *et al*., 2020).

1.2 Geopolymer Concrete Materials and their Composition

Geopolymer concrete source materials can be obtained from various amorphous forms of silicate and alumina bearing or source materials like industrial by-products, fly ash, blast furnace slag, silica fume, also combinations thereof (Lloyd and Rangan, 2009), or agricultural by-products, rice husk ash, groundnut shell ash, etc., naturally occurring clays (e.g. kaolin), etc.

Table-1 Chemical Composition of alumina-silicate source or bearing materials

Source Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O_3	LOI
Fly ash	40.00	25.00	6.00	20.00	3.71	1.74	0.80	0.96	3.00
GGBF Slag	40.00	13.50	1.8 0	39.20	3.60	0.20	0.20	-	-
Rice Husk– Ash	87.20	0.15	0.16	0.55	0.35	0.32	3.60	-	6.55
Metakaolin	50.67	46.89	0.39	1.47	0.10	-	0.19	0.081	0.57
Silica Fume	87.29	0.80	1.51	1.45	0.14	-	2.02	0.38	2.10
Palm Oil Fibre–Ash	51.18	4.61	3.42	6.93	4.02	-	5.52	0.06	21.60
Kaolin	52.00	35.00	1.00	< 0.05	0.70	-	2.00	0.05	
Dolomite	15.37	1.69	0.51	23.00	17.2	-	0.19	0.013	
Ground Nut Shell–Ash	16.21	5.93	1.80	8.69	6.74	-	15.73	9.02	
Corn Cob–Ash	66.38	7.48	4.44	11.57	2.06	-	4.92	0.41	
Sugar Cane Ash	62.43	4.38	6.98	11.8	2.51	1.48	3.53		4.73

[Dave *et al.,* 2017; Hariz and Mohd, 2017; Raheem *et al*., 2010; Nwofor and Sule, 2012]

The chemical compositions of some frequently used GPC source materials are shown in Table-1, and the major compounds in the source materials are silica (SiO_2), alumina (Al_2O_3), iron (ii) oxide (Fe_2O_3) and calcium oxide (CaO). Their ranges of their compositions are 15-90, 0-50, 0-10 and 0-40 percents respectively, with average mean/median quantities found to be 51.2/51.7, 6.0/13.2, 1.7/2.6, 10.1/12.5 respectively. Also present in smaller quantities are magnesium oxide (MgO), sulphate (SO_3), potassium oxide (K_2O), sodium oxide (Na_2O), etc, their average combined content is less than 10 percent, and organic content is generally less than 5 percent.

1.3 Characteristics and Performance of Geopolymer Concrete

Geopolymer concrete posses better workability, chloride penetration and acid resistances, also low creep and shrinkage (Somiyadevi and Aruna, 2019). It possesses good weathering resistance (Lee et al., 2019), and has better structural performance in respect of static and dynamic loading and blast loadings as compared to Portland cement concrete (Qingfei et al., 2019; Kumaravel and Thirugnanasambandam, 2013). Water absorption and abrasion resistance increased and reduced respectively with heat levels above room temperatures with associated compressive strength losses of about 50 and 75 percents at 400 and 800^{o}C respectively (Gambo et al., 2020). The enhanced mechanical properties of geopolymer concrete are due to the formation of aluminosilicate amorphous phase in a three-dimensional network with a fully compact and cohesive matrix in the microstructure of the material (Li, 2019). Crack patterns and failure modes observed in geopolymer concrete beams were similar to the cement concrete beams (Kumaravel and Thirugnanasambandam 2013, Deivabalan and Manigandan 2015), but the elastic modulus is lower than that of Portland cement concrete for similar compressive and tensile strengths (Cui et al., 2020), therefore presumptive values of elastic modulus from standard specifications for Portland cement if adopted will be misleading.

1.4 Development of Hybrid Geopolymer Concretes

Silica source materials combinations can optimise and enhance the properties of the geopolymer concrete beyond the performance of primary source concrete. The replacement of 30 percent fly ash with low calcium waste wood ash (Arunkumar et al 2021) optimized the workability and mechanical properties over long curing periods, but optimized performance was achieved with 50–60 percent replacement with high calcium wood waste at earlier ages (Ban and Ramli, 2012). Venkateswararao et al. (2013) preferred to call their blends geopolymer concrete composites (GPCC) and they found that product and strength qualities could be moderated by adjusting the compositions of the source materials. Binary combinations of fly ash and ground granulated blast furnace slag optimised the concrete properties for 80 and 20 percents compositions respectively (Venkateswararao et al., 2013), although flexural strengths of composites were relatively lower than the primary geopolymer concretes at early ages but were reversed and became much higher at maturity durations of 28 days. In a study involving hybrid combinations of fly ash and ground granulated blast furnace slag (Somiyadevi and Aruna, 2019) enhanced optimal compressive and flexural strengths were obtained at 50/50 combination. Incorporating calcium rich slag in fly ash geopolymer concrete enhanced early age strength developments at 3 and 7days which were about 50-75 and 80-93 percents respectively of the 28 days compressive strengths (Sasi and Sumathy, 2021). Also, ternary blends involving fly ash as base silica source material and replacement with ground granulated blast furnace slag and high-magnesium nickel slag showed that replacements of 20 and 10 percents respectively resulted in 100 and 58 percents increase in the 28-day compressive and splitting tensile strengths respectively (Li, 2019). Ultra-high-performance geopolymer concretes cured at ambient temperature have been developed (Ambily et al., 2014) by combining ground granulated blast furnace slag and silica fume, compressive and flexural strengths of 124.0 and 9.1 MPa respectively were realised, the strengths were further enhanced with steel fibres to 175.0 and 12.0 MPa respectively. This study, therefore examines hybrid geopolymer concrete compounded from blends of fly ash, kaolin and rice husk ash which are the most probable raw material sources of alumina-silicates in Nigeria, and have nonetheless received only limited attention.

2. METHODOLOGY

The raw materials used in this study were checked against the approved standards. Table-2 shows the geopolymer concrete materials in the various assessments of this study. Samples of fly-ash, kaolin and rice-husk were procured after which relevant chemical analysis were conducted. The fly ash was obtained from Enugu, while the rice husk ash was obtained from rice milling factories at Ekpoma in Edo State, and kaolin was excavated from mines at Ikpeshi, also in Edo State.

Table-2 Raw Materials, Description and Place of Procurement

Raw material	Description
Fly-Ash, Kaolin Rice-Husk Ash (RHA)	The rice husk was then burnt (with RHA, Fly Ash and Kaolin) sieved through 600μm sieves
Sodium Hydroxide Solution Sodium Silicate Solution	Sodium hydroxide solution with 97-98% purity and 14M molarity; Sodium silicate solution with Modulus (Ms) of 2.0.
Limestone Portland Cement	Limestone Portland cement conforming to (BS12-1:1996)
Aggregates	crushed coarse aggregates with nominal maximum size of 20mm and natural fine aggregates
Water	Deionized water used to dissolve sodium hydroxide and sodium silicate, potable water for Portland cement concrete.

The investigations were carried out in stages involving different experiments, tests and analyses. Index material evaluations were conducted on the fine and coarse aggregates, which were river sand and crushed granitic rocks respectively. The chemical compositions and specific gravities of the alumina-silicate source materials (fly ash, kaolin and rice husk ash) were determined. The binary blends of source materials utilised fly ash as the base material and replaced with 10 and 20 percents each of kaolin and rice husk ash in separate assessments, but for the ternary blends kaolin and rice husk ash were combined in equal proportions and used to replace 10 and 20 percent of the fly ash base material. Static compressive and flexural tensile tests conducted at designated maturity durations.

2.1 GPC and OPC Concrete Mix Design and Materials Calculation Estimate

The Geopolymer concrete mixtures were designed using a mix procedure developed by (Rangan, 2008), although optimised mixture combinations utilising the Taguchi procedure can been used to determine mixture compositions (Ahmed Al - Dujaili et al., 2020) which reduces the tedious trial and error procedures in mixture formulations (Lahoti, et al., 2017). The modified parameter of alkaline/source material ratio was utilized in this study. The Alkaline to Source Material (Al/SM) and silicate to alumina (Si/Al) ratios are provided in Table-3. Also, the water to solid (W/S) ratios were between 0.20 and 0.24. The geopolymer concrete was produced by mixing the dry aggregates (fine and coarse) with alkaline solutions (sodium hydroxide and sodium silicate) in a mixing pan. The fresh mixture was then cast into the required moulds (100mm x 100mm x 500mm beams and 150mm x 150mm x 150mm cubes) which were coated with a releasing agent (oil) to prevent the mix from sticking to the mould. The freshly cast samples were cured in a thermostat controlled kiln for 10 hours at an average temperature of 70 degree Celsius, since strength and density are enhanced with hot curing of geopolymer concrete specimens, and compressive strength of hot cured sample are about two times the strengths of ambient cured samples (Vijai et al., 2010). Water curing is counterproductive to strength gain and should not be adopted for geopolymer concrete (Qureshi et al., 2021). The samples were demoulded 24 hours after the oven curing and thereafter left to be air cured for varying maturity durations.

The Portland cement concrete (control samples) was prepared at water/cement and aggregates/cement ratios of 0.50 and 5.17 respectively in a pan mixer after which the fresh mixtures was cast into oil coated moulds (100mm x 100mm x 500mm beams and 150mm x 150mm x 150mm cubes).

Table-3 Geopolymer concrete mixture proportions

Mix	A/S	W/S	AL/SM	Aggregate (Kg/m^3)		Source Material (Kg/m^3)			Water	Alkaline (kg/m^3)	
				Coarse	Fine	FA	Kaolin	RHA	(Kg/m^3)	NaOH	Na_2SiO_3
FA	3.90	0.22	0.35	1201	647	408	–	–	20.7	41	103
Kaolin	3.90	0.20	0.35	1201	647	–	408	–	16.5	41	103
RHA	3.90	0.23	0.35	1201	647	–	–	408	25.8	41	103
FKA	3.50	0.22	0.35	1170	630	399.6	44.4	–	25.8	44	111
FKB	3.50	0.22	0.35	1170	630	399.6	44.4	–	25.8	44	111
FRA	3.90	0.24	0.40	1170	632	354.6	–	39.4	23.0	45	113
FRB	3.90	0.24	0.40	1170	632	354.6	–	39.4	23.0	45	113
FRKA	3.90	0.23	0.45	1201	647	342.9	19.1	19.1	25.8	49	122
FRKB	3.90	0.23	0.45	1201	647	342.9	19.1	19.1	25.8	49	122
FRKC	3.90	0.23	0.45	1201	647	342.9	19.1	19.1	25.8	49	122

Note: A/S =Aggregate/Solid ratio, W/S = Water/Solid ratio, AL/SM = Alkaline Liquid/Source Material ratio; Control = Ordinary Portland cement
FKA & FKB = Samples containing percentages of Fly-Ash and Kaolin
FRA & FRB = Samples containing percentages of Fly-Ash and RHA
FRKA, FRKB & FRKC = Samples containing percentages of Fly-Ash, RHA and Kaolin

The samples were demoulded after 24 hours and thereafter placed in a curing bath, the beam and cube samples cured for 28 days durations before being subjected to destructive tests. Flexural strength tests were carried-out on both OPC and GPC concrete samples and were conducted in accordance with the relevant codes (BS1881-116:1983; BS1881-118: 1983).

3. RESULTS AND DISCUSSION

The experimental investigations involved in this study included aggregate assessments, chemical characterisation and alkali activation of alumina-silicate source materials in ascertained blends, water and kiln curing of the Portland cement and geopolymer concrete test sample cubes and beams and subsequent static destructive tests conducted on them. The results of the various tests and analyses are presented and discussed as follows:

3.1 Physical and chemical properties of aggregates and alumina-silicate materials

The specific gravities of the fine and coarse aggregates are 2.65 and 2.70 respectively. The particle size distributions are shown in Table-4. The coarse aggregates maximum size was 20mm. The specific surface areas of the fine, coarse and combined aggregates estimated from the grading modulus (Jackson and Dhir, 1988) are 502.49, 19.21 and 258.27 m^2/kg respectively. The specific gravity and specific surface area are of the Portland cement were 2.96 and 365 m^2/kg respectively.

Table-4 Particle size distribution of aggregates by percentage passing sieve sizes

Sieve sizes (mm)	10.000	5.000	2.360	1.180	0.600	0.300	0.150	0.075
Fine aggregates	100.00	100.00	97.43	83.09	54.08	16.21	2.20	0.16
Coarse aggregates	17.45	0.75	0.24	0.05	0.05	0.05	0.05	0.05
Combined aggregates	58.86	50.51	48.97	41.80	27.30	8.36	1.35	0.33

Table-5 Chemical constituents of the mineral source materials in percentage

Constituent and nomenclature		Industry ID	Fly-Ash	Kaolin	Rice husk ash
Silicon dioxide	SiO_2	Silica	62.10	46.20	88.32
Aluminum oxide	Al_2O_3	Alumina	27.44	39.20	0.46
Iron (III) oxide	Fe_2O_3	Ferric oxide	4.57	0.23	0.67
Titanium dioxide	TiO_2	Titania	1.09	0.09	–
Calcium oxide	CaO	Quicklime	0.83	0.06	0.67
Magnesium Oxide	MgO	Magnesia	0.55	0.07	0.44
Sodium oxide	Na_2O	Anhydride of NaOH	0.04	0.09	0.12
Potassium oxide	K_2O	Caustic potash	1.17	0.21	2.91
Weight loss on ignition	LOI	Organic content	0.76	13.80	5.81

The results of material characterisation tests carried out on the alumina-silicate source materials are provided in Table-5. The dominant chemical components in the fly ash and kaolin are silicon dioxide (silica- SiO_2) and aluminum oxide (alumina- Al_2O_3) with proportions of 62.10 and 27.44 percents respectively for the fly ash, also 45.20 and 39.20 percents respectively for kaolin, and combined proportions of 89.54 and 84.40 for fly ash and kaolin respectively. While for rice husk ash the dominant component is silica at 88.32 percent. The minor minerals identified are Fe_2O_3, TiO_2, CaO, MgO, Na_2O, K_2O had total compositions of 8.25, 0.75 and 4.81 percents for fly ash, kaolin and Rice husk ash respectively. However, 1.45, 0.05 and 0.60 percents masses respectively are uncounted for fly ash, kaolin and Rice husk ash respectively. The organic contents are 0.76, 13.80 and 5.81 percents respectively. The high organic content in kaolin could have resulted since the source material was not subjected to calcinations and transformed to metakaolin. The specific gravities of fly-ash, kaolin, rice husk ash are 1.93, 2.31 and 1.51 respectively.

3.2 Rheological properties of the fresh Portland cement and geopolymer concrete mixtures

The workability of the fresh concrete mixtures was determined by slump measurements (Table-7). The Portland cement concrete mixture had a slump of 14mm, but for the primary source and binary hybrid geopolymers the slump reduced marginally to an average of 13mm, and for ternary hybrid geopolymer mixtures the workability was between 11 and 12mm.

Table-6 Workability and setting time assessments

Concrete Samples		Slump (mm)	Setting time (minutes)	
			Initial	Final
Portland cement concrete	OPC	14	122	183
Primary geopolymers	Fly ash	13	74	164
	Kaolin	12	133	194
	RHA	14	92	153
Binary hybrids geopolymers	FKA	13	79	167
	FKB	12	85	170
	FRA	13	75	162
	FRB	13	77	161
Ternary hybrids geopolymers	FRKA	12	76	164
	FRKB	11	81	165
	FRKC	11	84	165

Although, both concretes may be described to having workabilities within the same range, but the typical and consistent reductions in the geopolymer concretes may indicate that geopolymer concretes may be more plastic than Portland cement concretes. The Portland cement and geopolymer concretes setting times are also shown in Table-6.

The initial and final setting times for Portland cement concrete are 122 and 183 minutes, except for kaolin based geopolymer concrete with initial setting time of 133 minutes, the other single, binary and ternary geopolymer concrete mixtures have a range for initial setting time to be 74 to 92 minutes, with an average of 80 minutes which is about two-third of the initial setting time for Portland cement concrete. The final setting time for Portland cement concrete is 183 minutes, which is just less than the final setting time for kaolin based geopolymer concrete of 193 minutes, however, the final setting times for other geopolymer concretes are between 161 and 170 minutes. The recommended standards for the minimum initial and maximum final setting times are 45 and 600 minutes respectively (BS12:1996). Therefore, all the samples are within the limits of specifications criteria and are therefore appropriate.

3.3 Compressive strength

The compressive strength test results are illustrated in Figure-1. The results are indicated for Portland cement concrete, also for various primary, binary and ternary combinations of fly ash, kaolin and rice husk ash.

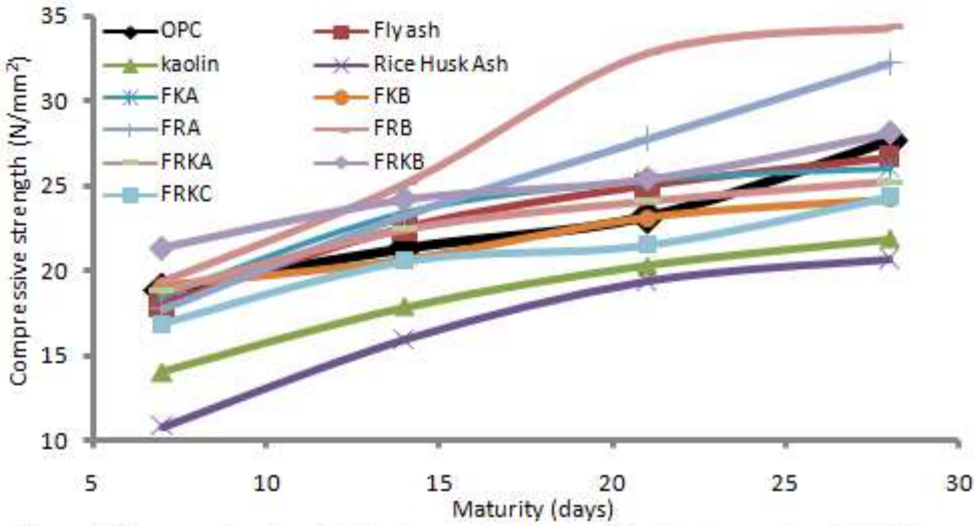

Figure 1: Compressive strength development patterns of Portland cement and hybrid geopolymer concretes

The compressive strength and development patterns of the fly ash geopolymer concrete is similar to that of the Portland cement concrete, the 28days compressive strength of the fly ash and Portland cement concrete are 26.67 and 27.63 N/mm^2 respectively, with insignificant difference. But the other primary bearing materials of kaolin and rice husk ash with compressive strengths of 21.90 and 20.70N/mm^2 respectively are just about 60 percent of the compressive strength of the Portland cement and fly ash geopolymer concretes.

The binary blends of the source materials of fly ash/kaolin and the ternary blend of fly ash/rice husk ash/kaolin all have similar strength and development patterns with the Portland cement concrete, although they are characteristically higher than the primary rice husk and kaolin geopolymer concretes. The best performing geopolymer concrete mix is the fly ash and rice husk blends which had a higher rate of strength development and a 28days compressive strength of 33.28N/mm^2 which is 20.50percent higher than the Portland cement concrete.

3.4 Flexural tensile strengths

The flexural tensile strengths from test beams compounded from various mix combinations of the different source materials are provided in Table-**7** and illustrated in Figure-**2**. The flexural tensile strengths are nonlinearly proportional to the compressive strengths, and this is without regard to whether the material is either Portland cement or geopolymer concrete product. The flexural tensile strength of the Portland cement concrete was 5.49 N/mm^2 at 28days. The effects of primary silicate source materials on product flexural strengths vary widely. Rice husk ash had the least strength with 0.78 N/mm^2 followed by kaolin with about twice as much strength of 1.65 N/mm^2. Fly ash geopolymer concrete had the highest primary source material strength with a spike of 4.11 N/mm^2. The binary and ternary combinations of source materials produced geopolymer concretes with improved flexural tensile strengths but the binary combination of fly ash and rice husk ash produced concrete with the highest flexural tensile strength of 5.85N/mm^2, which is higher than the flexural strength of the Portland cement concrete. The compressive and flexural tensile strengths can be closely correlated by the nonlinear relationship described in Equation-1.

$$f_{tm} = 0.375 + 0.665(f_c - 20)^{0.875} \qquad 1.$$

The features of this expression are such that a concrete with strength of 20N/mm^2 would have a tensile strength of 0.375N/mm^2. Conversely, the minimum compressive strength of the geopolymer concrete for which the tensile strength is zero is 19.51 N/mm^2. The equation therefore has a practical minimum limit of significance for compressive strength of 20.0 N/mm^2, and compressive strengths above 30 N/mm^2 may have their tensile strengths overestimated, for example, the product of the fly ash and rice husk ash binary combination would have an estimate of 8.069 N/mm^2 from this expression against the experimental and trend line interpolation of 5.85 and 6.019N/mm^2 respectively.

Characteristic strength has been determined assuming a standard deviation of a quarter of the characteristic strength and adopting statistical 95 percent confidence limits, and the plot is also provided in Figure-2 and described by Equation-2, and with an assumed material safety factor of 1.50 the design strength had also been obtained.

$$f_{tk} = 0.267 + 0.475(f_c - 20)^{0.875} \qquad 2.$$

Therefore, the characteristic flexural tensile strength of a geopolymer concrete with compressive strength of 20 N/mm^2 would be 0.267 N/mm^2.

Table-7 Flexural tensile strengths of test cubes and beams in N/mm^2 at 28days

Sample	Mean Strengths		Trend Line Estimates of Flexural Strength		
	Compression	Flexure	Experimental	Characteristic	Design
PC Concrete	27.63	5.49	5.49	3.786	2.524
Fly-Ash	26.670	4.110	4.070	2.807	1.871
Kaolin	21.900	1.650	1.535	1.058	0.706
Rice Husk Ash	20.700	0.930	0.804	0.554	0.370
FKA	26.030	3.390	3.765	2.596	1.731
FKB	24.200	2.010	2.831	1.953	1.302
FRA	32.230	5.580	6.279	4.331	2.887
FRB	34.330	6.120	6.905	4.762	3.175
FRKA	25.230	3.000	3.367	2.322	1.548
FRKB	28.130	5.310	4.728	3.261	2.174
FRKC	24.370	1.290	2.922	2.015	1.343

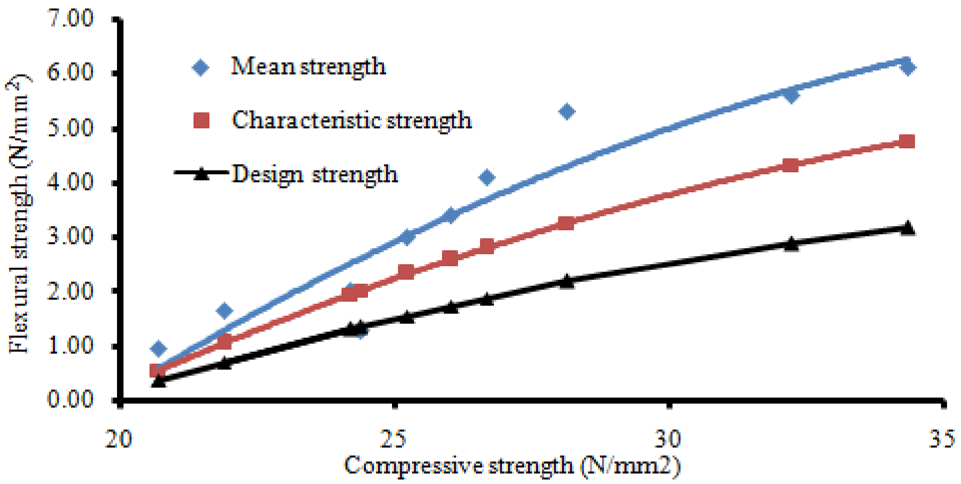

Figure 2: Flexural tensile strengths of hybrid geopolymer

Because of the probable overestimations at high compressive strengths the best outcomes for Eqnuation-2 in prescribing flexural strengths would be for concretes with compressive strengths between 20 and 30 N/mm^2, or possibly extended to compressive strength 40 N/mm^2, which is a few units above the range covered in this study, the possible errors would have been compressed by the statistical evaluation for confidence and the further factor of safety needed to derive the design strength.

3.5 Influence of relative amounts of silica and alumina on strength characteristics

From the various source materials outlined in Table-1 there is a pattern of low alumina at the extremes of silica contents (Figure-3), the alumina content rises steadily for increasing amounts of silica until maximum content of alumina of about 45 percent at silica content of about 50 percent. The alumina content drops rapidly for source materials with silica of more than 50 percent. Therefore, there are probable silica contents for which the alumina contents are optimised. The other metallic oxides of iron, calcium, magnesium, sulphur, potassium, and sodium are present in small and varying amounts.

Based on the typical varying nature of the alumina content a categorisation maybe devised for the bearing materials with respect to the silica content as shown in Figure-3. Four categories can be identified as shown in Table-10 deduced from the data provided in Table-1, and the categories are: very high, high, medium and low classifications. Almost all the agricultural wastes and rocks have alumina contents less than 10 percent. The industrial wastes (fly ash and GGBF Slag) and clay sources (Kaolin and Metakaolin) are within the silica ranges of 35-55 percent and they have the highest alumina contents of between 15 and 45percents. Kaolin and fly ash involved in this study have medium content silica content which is within 35 and 55 percents; rice husk ash is in the grouping with very high content of silica of between 75 and 100 percents. The medium clay sources are almost entirely silica and alumina in approximately equal proportions, while the industrial sources have appreciable amount of calcium oxides (greater than 20 percent). Very high category is essentially pure silica sources like rice husk ash and silica fume; high and low categories have significant amounts of calcium oxides and secondary oxides of potassium and magnesium.

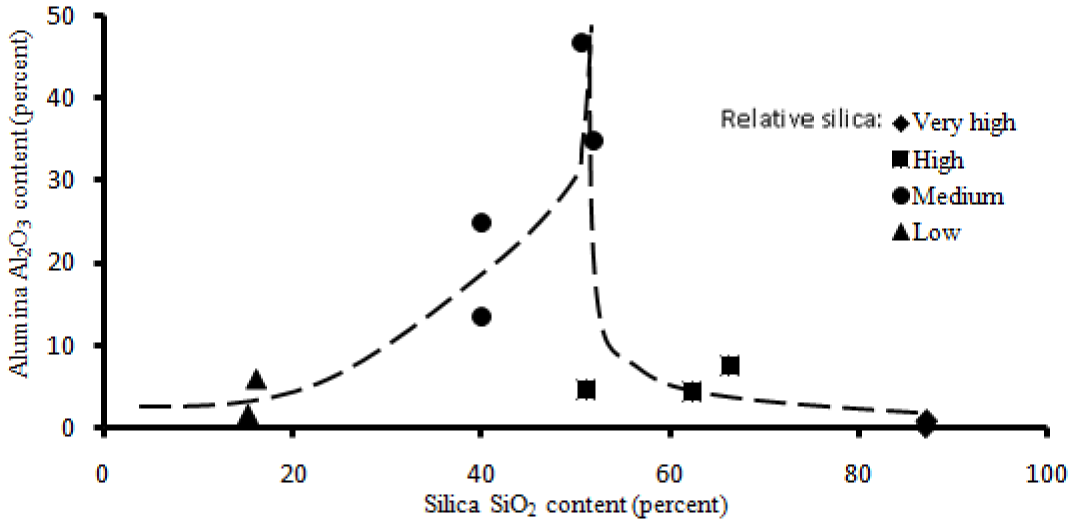

Figure 3: Relative amounts of silica and alumina contents in bearing source materials

Table-8 Categorization of bearing materials on the basis of silica content in percent

Category	Silica content	Bearing materials
Very high	70-100	Rice Husk Ash, Silica Fume, etc.
High	55-70	Palm Oil, Fibre–Ash, Corn Cob–Ash Sugar Cane Ash, etc.
Medium	35-55	Metakaolin, Kaolin, Fly ash, GGBF Slag, etc.
Low	10-35	Dolomite, Ground Nut Shell–Ash, etc.

Based on the mixture combinations (Table-3) and chemical compositions of the source materials (fly ash, kaolin and fly ash) utilised in this study as provided in Table-**5** the respective compositions of silica and alumina contents in each source material, also in the binary and ternary mixtures are provided in Table-**9**. The silica and alumina in the source materials are within 60-90 and 0-40 percents respectively, but, the proportions of the silica and alumina in the blended binary and ternary hybrid mixtures are within the narrowed range of approximately 60-68 and 22-30 percents respectively. The silica/alumina ratios for fly ash and kaolin are 2.263 and 1.179, but spiked to 192.0 for rice husk ash because of the almost negligible amount of alumina. The silica/alumina ratios for the binary and ternary hybrid mixtures were estimated to be between 1.977 and 3.055. The source materials utilised in this study are kaolin, rice husk ash and fly ash, which are clay minerals, agricultural and industrial wastes respectively. Why rice husk ash has very high silica content, kaolin and fly ash have medium silica content.

Table 9: Percentage Composition of Silicate to Aluminate Ratio

Mix type	Mixture composition (percent)			Mineral (percent)		Silica/Alumina Ratio
	Fly ash	Kaolin	RHA	SiO_2	Al_2O_3	
Fly-Ash	100			62.10	27.44	2.263
Kaolin		100		46.20	39.20	1.179
Rice Husk Ash			100	88.32	0.46	192.000
FKA	90	10		60.51	28.62	2.114
FKB	80	20		58.92	29.80	1.977
FRA	90		10	64.72	24.74	2.616
FRB	80		20	67.34	22.04	3.055
FRKA	90	5	5	62.62	26.68	2.347
FRKB	80	10	10	63.13	25.92	2.436
FRKC	70	15	15	63.65	25.16	2.530

The plots of the silica/alumina ratios in the primary sources and hybrids of binary and ternary combinations of source materials against compressive strengths (Figure-4) and flexural tensile strengths (Figure-5) show typical trends of rising levels of strengths with increasing values of silica/alumina ratios regardless of the nature of hybrid material combinations. The minimum silica/alumina ratio of 1.20 corresponds to whole base or primary source material of kaolin with compressive and flexural tensile strengths of 21.90 and 1.65 N/mm^2 respectively. The pattern progresses through varying gradients until the silica/alumina ratio of 3.10 corresponding to maximum attainment of compressive strength and flexural tensile strengths of 34.33 and 5.31 N/mm^2 respectively for fly ash/rice husk ash hybrid of 80/20 composition. The strengths of the binary blends are expectedly between the respective extreme whole fractions. The compressive and flexural tensile strengths for whole rice husk ash geopolymer concrete are 20.70 and 0.93 N/mm^2 which are the minimum recorded values even at silica/alumina ratio of 192.0; this relative excessive value could not be conveniently located on the charts. The trend of strength progression with active positive gradient at the silica/alumina ratio of 3.10 may suggest that maximum strengths will be achieved at an optimal silica/alumina ratio somewhere between 3.10 and 192.0. However, beyond alumina/silica ratio of 2.10 there is a spur of reducing compressive and flexural tensile strengths for ternary blends involving combined substitutions of 10 and 30 for kaolin and rice husk ash in equal proportions of 5 and 15 percents each, but the combined substitution of 20 percent with 10 percent each of kaolin and rice husk ash produced relative higher strengths that fell into the general trend paths of increasing strengths development.

Low calcium wood waste ash had been reported to have optimized fly ash based geopolymer concrete at a substitution level of 20 percent, other investigations also reported optimizations at substitution rates of between 20 to 35 percents, although high calcium materials optimized the fly ash geopolymer concretes at significantly higher substitution level of as much as 55 percent.

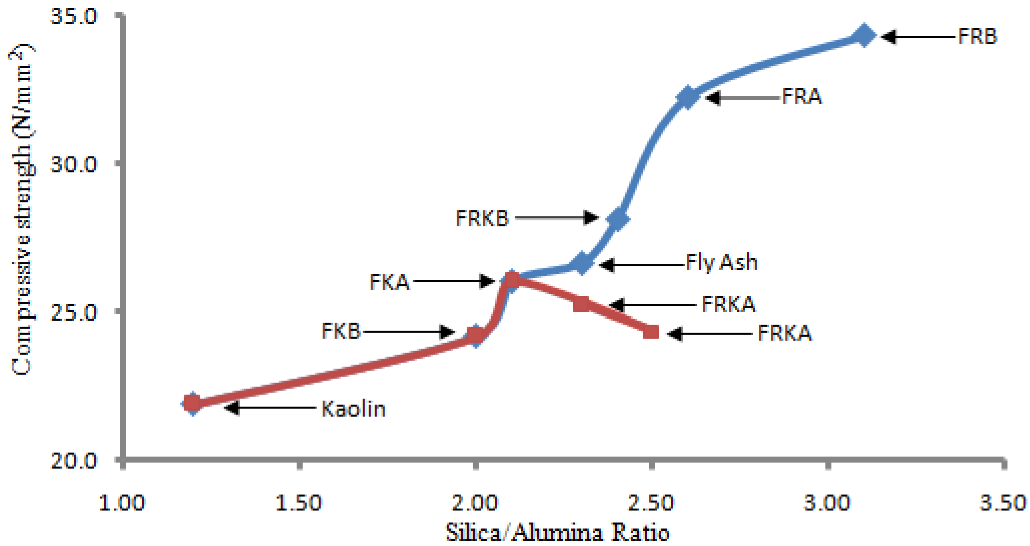

Figure 4: Effects of relative amounts of silica and alumina in hybrid combinations of source materials on the 28-day flexural tensile strengths of geopolymer concrete

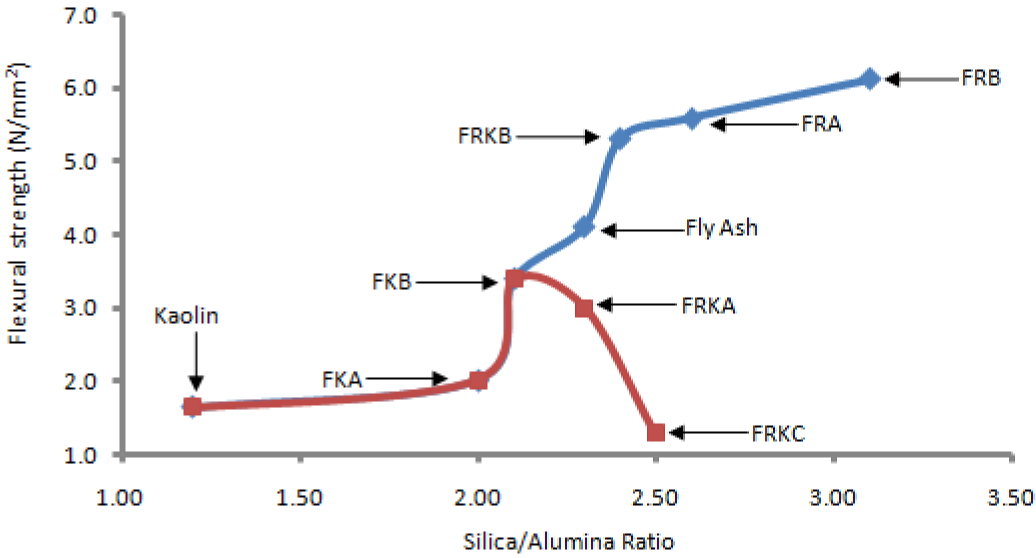

Figure 5: Effects of relative amounts of silica and alumina in hybrid combinations of source materials on the 28-day compressive strength of geopolymer concrete

Rice husk ash being a very low calcium source material will be projected to optimise fly ash geopolymer concretes at substitution levels of between 25 and 35 percents, or at an average of 30 percents percent when the silica and alumina proportions are approximately 70.0 and 19.4 respectively, and the silica/alumina ratio would be 3.617. Therefore, the silica/alumina ratio should be a primary influence parameter in determining mix proportions suitable for desirable geopolymer concrete performance and operational characteristics. The possible significance of secondary effects of other oxides present in the source materials in quantities assumed to be negligible was not an objective of this study, however, it has been determined that increases of sodium oxide concentrations in alkali activated silica concretes raised the levels of compressive strength, workability and shrinkage, while it reduces initial and final setting times, and lowers water absorption (Allahverdi *et al*. 2010; Shukla *et al*. 2020). Although the optimal balance in terms of the silica/alumina ratio may have been achieved for hybrids involving fly ash and rice husk ash with respect to the highest strengths performances, but the source material also had the highest sodium oxide content at 0.12 percent.

4. CONCLUSION

This study has investigated the prospects of combining different silica source materials for the production of geopolymer concretes. The results have shown that fly ash geopolymer concrete recreates or reproduces the compressive characteristics of the Portland cement concrete; the strength properties of primary geopolymer concretes of rice husk ash and kaolin are distinctively lower than the Portland cement concrete. Binary combinations of fly ash/kaolin and ternary combinations of fly ash rice husk ash/kaolin have near Portland cement concrete properties. However, the best performing combination of source materials is the fly ash/rice husk ash blends which had a higher rate of strength development and with an increase of 20.5ercent over the compressive strength of the Portland cement concrete at 28 days. The flexural tensile strengths also show the same patterns of strength development with the maximum flexural strength of 5.85 N/mm^2 being that for fly ash/rice husk ash binary blended geopolymer concrete. it has been determined that regardless of the source material type and nature of blending the silica/alumina ratio will be critical to mixture selections or designs as it brings all the primary and hybrid geopolymer concretes into a unified pattern of strength development. This study has shown that geopolymer concretes developed from industrial and agricultural wastes, also from natural occurring clays may have comparable properties with those of Portland cement concretes, it has also been demonstrated that by adjusting the compositional characteristics of the blends of silicate source materials higher performance geopolymer concrete relative to Portland cement concrete could be obtained.

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