Exploring Relative Mass Mix Design in Compressive Strength Investigation of Calcined Clay Geopolymer Concretes (CCGC) – A Preliminary Investigation

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ABSTRACT
The compressive strengths of CCGC samples were studied by adopting the mass proportioning approach in the design of the cement mix. Calcined clay (CC) was adopted as the precursor with alkali activator solution. CC was combined with the activating media in mass proportions of 70:30, 60:40, and 50:50 respectively. The activating media consists of NaOH and Na_2SiO_3 with the proportions of the activating media further split into two mass ratios in steps of 10, making 15 binder mixes - 70:30:0, 70:20:10, 70:10:20 and 70:0:30 (CC: NaOH:Na_2SiO_3) in the 70:30 group; 60:40:0, 60:30:10, 60:20:20, 60:10:30 and 60:0:40 in the 60:40 group; and 50:50:0, 50:40:10, 50:30:20, 50:20:30, 50:10:40, 50:0:50 in the 50:50 group. For each set of binder mixes, four NaOH molar solutions – 10, 12, 14 and 16M, were adopted with corresponding geopolymer mixes designated CCGC-10, CCGC-12, CCGC-14, and CCGC-16, respectively. Grade M20 concrete samples (150mm cubes) were prepared with these binders and tested. Results show that the compressive strengths generally increase with concentration of the alkali activator solution, up to the optimum at 14M NaOH. Maximum 28-day strengths for the CCGC-10 (9.54N/mm^2) and CCGC-12 (10.74N/mm^2) occurred with the mix 50:10:40 while 60:10:30 mix was responsible for CCGC-14 (13.35N/mm^2), and CCGC-16 (5.26N/mm^2). Curing at elevated temperature for strength enhancement was recommended as possible areas for further studies.
Keywords: Calcined Clay, Geopolymer Concrete, Compressive Strength

I. INTRODUCTION

Geopolymer systems are alternative binding systems presently attracting interests in the construction industry. Considering that Portland cement is responsible for about 85% of the energy and 90% of CO_2 emissions attributed to preparation of concretes [1, 2], the need to improve on cost-effectiveness and reduce global carbon footprints propel research efforts in investigating various geopolymer systems as alternative binder systems.

Geopolymer systems have been found to offer comparable properties to Portland cement systems; principally their low energy requirements and CO_2 emissions [3, 4]. Besides, Compressive strengths of geopolymer cements have been reported as similar to those of Portland cement [5], and higher with curing at elevated temperatures [3]. It also shows better thermal stability at higher temperatures [3] and improved abrasion resistance [6] compared to Portland cement systems.

Geopolymer systems are produced from the dissolution of a precursor material in an alkaline activating solution leading to polymerization into molecular chains and networks to create the binding phase [2, 3]. The precursors are minimally processed natural materials or industrial byproducts rich in oxides of silicon and aluminum which reacts with the alkali solutions to initiate a process similar to the hydration of cement. This explains why geopolymers are referred to as alkali-activated or inorganic polymer cements [2, 3].

Aside the need to decide on the appropriate activator and its concentration, optimum proportioning of the geopolymer constituents becomes essential in the design of the geopolymer mix. A number of approaches have been proposed. Some range of ratios of major constituent oxides to yield optimum performance has been identified [2]. Water to solid ratio has also

been adopted for proportioning [7, 8, 9]; with the water of the alkali solution included in computing the water quantity.

Authors have presented and elucidated on different templates for proportioning. However, there have been shortcomings in these approaches of geopolymer mix design. Some authors who have proposed the same design template came up with different results. These approaches also appear to have technical complexities; making their adoption possibly unattractive for the end-users, especially those with inadequate technical orientation.

The possibility of proportioning geopolymer mixes by adopting relative masses of the constituent materials cannot be overlooked. This appears a simple and direct approach at proportioning geopolymers mixes for widespread use. It makes it more attractive to the local end-user who has been accustomed to such relative mass mix design in the application of Portland cement based mixes. This paper explores the adoption of this template for use in geopolymer concrete works. It investigates the compressive strengths of geopolymer concretes prepared with the adoption of alkali activated calcined clay as geopolymer cement.

II. METHODOLOGY

Material preparation

Calcined clay (CC) was prepared by calcining the natural kaolin clay at 750°C in the furnace for 1 hour as detailed in the author's previous works [10, 11, 12]. Sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) were adopted as activators, being most common and convenient alkali materials to handle [2, 13]. Sodium hydroxide of 98% purity was prepared into various molar solutions of 10, 12, 14, and 16M, respectively. Sodium silicate was obtained as gel, comprising of Na_2O (15.9%), SiO_2 (34.8%) and H_2O (49.3%). These were mixed to have a combined alkali solution (NaOHSi). The solution was prepared 24 hours prior to use as recommended by [2, 7].

The sand used is well cleaned and void of impurities, with grading ranging from 2mm down in tandem with the requirements of [14]. Similarly, granite was sized 19mm down as required in [14]. Distilled water was adopted for concrete mixing.

Preparation of Calcined Clay Geopolymer Concrete (CCGC) Samples

The calcined clay (CC) was combined with the activator (NaOHSi) in CC:NaOHSi mass ratios of 70:30, 60:40 and 50:50, respectively; for each of the four molar solutions of NaOH adopted. Being a mixture of two alkali solutions, the activator (NaOHSi) was proportioned by mass as detailed in Table 1, resulting to 15 different geopolymer cement mixes; for each of the four molar solutions of NaOH adopted. The mix design for grade M20 concrete was adopted for the CCGC and for control (Portland cement concrete).

Table 1: Geopolymer cement mix proportions for each NaOH Molar Solution

CC:NaOHSi Mix Ratios	Proportion of CC	Proportion of NaOH solution	Proportion of Na_2SiO_3 gel
70:30	70	0	30
		10	20
		20	10
		30	0
60:40	60	0	40
		10	30
		20	20
		30	10
		40	0
50:50	50	0	50
		10	40
		20	30
		30	20
		40	10
		50	0

If unit weight (kg) of the geopolymer cement, w_u is determined as:

$$w_u = a + b + c \qquad \dots 1$$

a, b and c represents the proportions of the NaOH solution, the Na_2SiO_3 gel, and calcined-clay components, respectively, per unit kilogram of the geopolymer cement

Then,

$$a = a_w + a_s \qquad \dots 2a$$

a_w and a_s = masses of the water and solid components of the NaOH solution, respectively, per unit kilogram of the geopolymer cement

$$a_s = a'_s * a / a' \qquad \dots 2b$$

a'_s = mass of NaOH pellets used in preparing molar solutions (e.g. 400, 480,..., 640g for 10, 12,…, 16M, respectively) while a' represents the final mass of the molar solution.

$$a_w = a - a_s \qquad \dots 2c$$

Also,

$$b = b_w + b_s \qquad \dots 3a$$

b_w and b_s = masses of the water and solid components of the Na_2SiO_3 solution, respectively, per unit kilogram of the geopolymer cement

$$b_w = 0.493 * b \qquad \dots 3b$$

(H_2O = 49.3% of Na_2SiO_3)

$$b_s = b - b_w \qquad \dots 3c$$

Therefore, the water-solid ratio of the geopolymer cement is detailed as:

$$0.5 = (a_w + b_w + e_w)/(a_s + b_s + c) \qquad \dots 4$$

e_w represents the mass of the excess water to be added to the geopolymer concrete mix

For each molar solution, 15 geopolymer cement mixes were prepared and each mix adopted to produce 150mm concrete cubes. These were air–cured for 7, 14, and 28 days, respectively. The samples prepared with 10M, 12M, 14M, and 16M NaOH solutions were designated as CCGC-10, CCGC-12, CCGC-14, and CCGC-16, respectively. The control samples (Portland cement concretes) were also cured under ambient conditions. Compression strength tests were carried out on the samples in line with the standards for compressive strength test.

III. RESULT

The result as presented in Tables 2a and 2b shows that the compressive strengths of the CCGC samples were generally not comparable with the strength of control. This has been largely attributed to the effect of curing temperature. Curing at elevated temperature enhances the strengths of geopolymer cements mixes [2, 3, 15, 16]. This work focuses on exploring the possibility of adopting relative mass proportions in preparing the geopolymer cement mix and is considered as preliminary investigation in this wise.

In any case, the results reflect the existence of a general pattern of compressive strength behaviours. The strengths of the CCGC samples generally increase with curing age and with concentration of the alkali activator solution. The concentration, in this wise, is described in terms of molarity and proportion of the alkali solution in the geopolymer cement mix. The strengths were found to increase with the molarity of NaOH solution, up to 14M. The strengths however dropped for the CCGC-16 samples. This generally agrees with previous authors [17, 18] Moreover, strengths increase with increasing proportion of the alkali solutions in the cement mix, up to optimum of 40% (that is the ratio 60:40 mix); noting also that, the higher the portion of Na_2SiO_3 of the two alkali material, the higher the strength of the resulting CCGC. This was aptly captured in Fig. 1 to Fig. 4.

Table 2a: Mean Compressive Strength of the CCGC Samples (N/mm^2) for CCGC-10 and CCGC-12

CC:NaOHSi Mix Ratios	CC:NaOH:Na$_2$SiO$_3$ mix proportion	CCGC-10 Curing Age			CCGC-12 Curing Age		
		7	14	28	7	14	28
70:30	70:30:00	1.07	1.28	1.35	1.39	1.66	1.70
	70:20:10	1.89	2.28	2.40	2.46	2.96	3.04
	70:10:20	2.61	2.79	2.94	3.39	3.63	3.72
	70:00:30	3.81	4.19	4.42	4.96	5.45	5.59
60:40	60:40:00	1.31	1.36	1.45	2.36	2.45	2.84

	60:30:10	2.05	2.52	3.54	3.68	4.53	6.94
	60:20:20	2.26	3.65	4.08	4.07	6.57	8.14
	60:10:30	4.11	4.65	4.71	7.63	8.62	9.23
	60:00:40	2.38	2.52	3.78	4.29	4.53	7.41
50:50	50:50:00	0.86	1.38	1.50	0.89	1.43	1.57
	50:40:10	0.89	2.20	2.97	0.92	2.28	3.11
	50:30:20	1.11	2.32	3.29	1.15	2.41	3.45
	50:20:30	2.08	6.37	6.69	2.16	6.61	7.00
	50:10:40	3.65	8.91	9.54	3.79	9.25	10.74
	50:00:50	0.93	1.79	4.03	0.96	1.86	4.22

Optimum 28-day strengths of the CCGC-10 samples align with the pattern already established; with the observed strength increasing due to increased alkali concentration, as anticipated. Figure 1 shows that, for the 70:30, 60:40 and 50:50 groups, the optimum strengths occurred with cement mixes 70:00:30 (4.42N/mm^2), 60:10:30 (4.71N/mm^2), and 50:10:40 (9.54N/mm^2) respectively. CCGC-12 samples had higher 28-day strengths with the optimum strengths occurring similarly for those prepared with 70:00:30, 60:10:30, and 50:10:40 cement mixes. These were 5.59, 9.23, and 10.74N/mm^2 respectively (Fig. 2).

Table 2b: Mean Compressive Strength of the CCGC Samples (N/mm^2) for CCGC-14 and CCGC-16

| CC:NaOHSi Mix Ratios	CC:NaOH:Na$_2$SiO$_3$ mix proportion	CCGC-14				CCGC-16		
		Curing Age				Curing Age		
		7	14	28		7	14	28
70:30	70:30:00	1.70	2.03	2.10		0.96	1.15	1.34
	70:20:10	3.00	3.62	3.82		1.70	2.05	2.43
	70:10:20	4.14	4.43	5.54		2.35	2.51	3.52
	70:00:30	6.06	6.66	7.83		3.44	3.78	4.98
60:40	60:40:00	3.58	3.71	4.11		1.07	1.11	1.62
	60:30:10	5.59	6.87	10.04		1.68	2.06	3.96
	60:20:20	7.61	12.29	13.22		2.28	3.69	5.20
	60:10:30	11.57	13.08	13.35		3.47	3.93	5.26
	60:00:40	6.51	6.87	10.72		1.95	2.06	4.22
50:50	50:50:00	1.07	1.71	2.10		0.99	1.58	1.99
	50:40:10	1.10	2.73	4.16		1.02	2.52	3.94
	50:30:20	1.38	2.88	4.61		1.27	2.66	4.37
	50:20:30	2.59	7.91	9.37		2.41	3.00	4.44
	50:10:40	4.54	11.07	11.64		2.81	3.32	4.79
	50:00:50	1.15	2.22	5.65		1.06	2.05	4.35
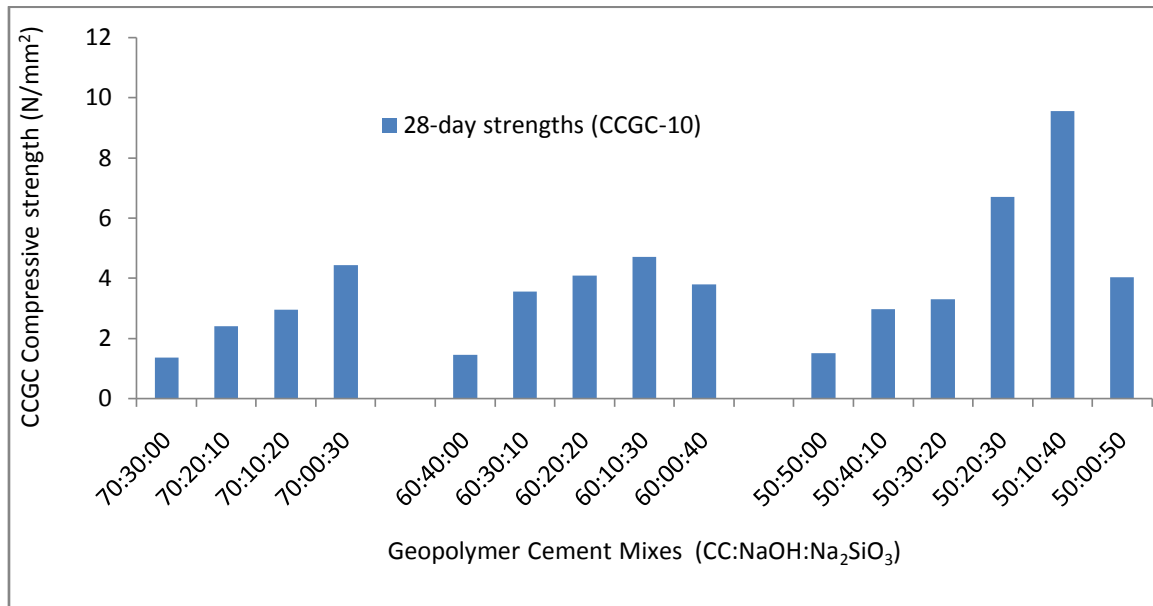
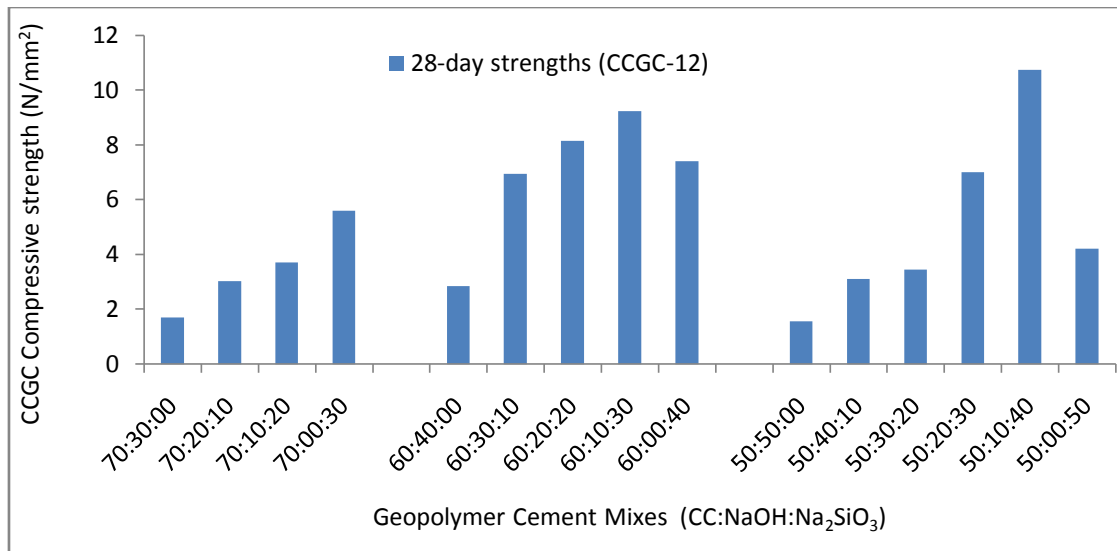Fig. 1: 28-day Compressive Strength for CCGC-10

Fig. 2: 28-day Compressive Strength for CCGC-12

Furthermore, the strengths of CCGC-14 samples were higher than other previous samples due to increased molarity, as earlier highlighted. Optimum strengths for the CCGC-14 cubes were 7.83. 13.35, and 11.64N/mm^2 adopting the 70:0:30, 60:10:30, and 50:10:40 mixes, respectively (Fig. 3). However, further increase in molarity saw a general decline in the compressive strengths. The CCGC-16 samples had optimum strengths of 4.98, 5.26, and 4.79 N/mm^2 for the 70:0:30, 60:10:30, and 50:10:40 mixes, respectively (Fig. 4).
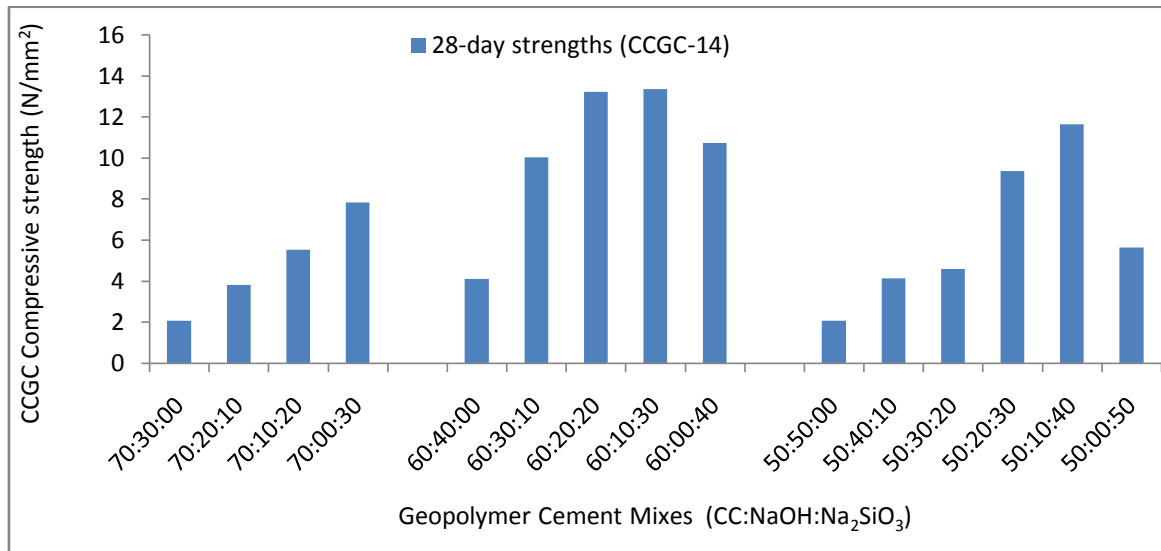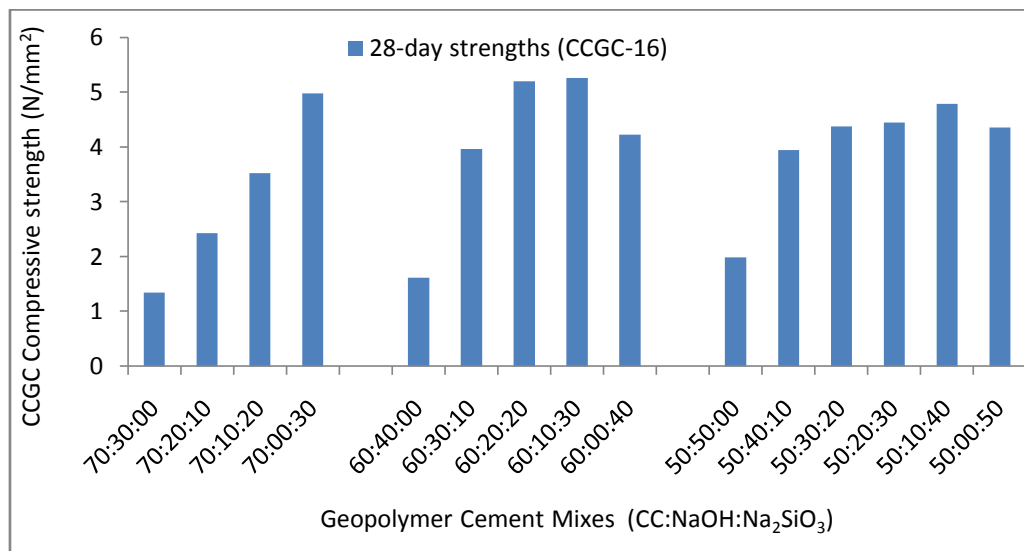
Fig. 3: 28-day Compressive Strength for CCGC-14

Fig 4: 28-day Compressive Strength for CCGC-16

Another interesting observation is that, for the CCGC-14 and CCGC-16 samples, the strengths of concretes in the 60:40 group were generally higher than the strengths of concretes in the 50:50 group. This was against what had been reported for concretes in the lower molarity groups. For the CCGC-14 samples, the 60:40 group had optimum strength of $13.35 N/mm^2$ whereas this dropped to $11.64 N/mm^2$ for the 50:50 group. Corresponding strengths for the CCGC-16 groups were 5.26 and $4.79 N/mm^2$, respectively. This observation had also been attributed to increased alkali content. The effects of increased alkali concentration through increased molarity (14 and 16M respectively) have reached its optimum impact such that increasing the alkali proportion in the cement paste (from

60:40 to 50:50) is of no use. Thus, strength dropped as a result.

The variation of the compressive strengths of the CCGC samples with molarity was aptly captured in Fig 5. The 70:0:30, 60:10:30, and 50:10:40 cement mixes yielded the optimum strength for the concretes in their corresponding groups 70:30, 60:40, and 50:50, respectively. The variations of the strengths of these cement mixes were captured as NaOH molarity is varied. As earlier noted, the strengths generally increased with molarity up to 14M and drops at 16M. Of the three mixes, the 70:0:30 cement mix returned the lowest set of strengths while the highest set of strengths were reported for concretes prepared with the 50:10:40 mix; up to 12M NaOH. At about 14M

NaOH, the concrete strength attributed to the 50:10:40 mix dropped while the 60:10:30 mix produced the highest strength. The twist in the instance of the 14M CCGC samples have been explained as due to increased overall alkali concentration/proportion in the 50:10:40 cement mix relative to the overall concentration/proportion in the 60:10:30 cement mix. The concentration in the 50:10:40 is perceived to have been more than the optimum needed for the best strength. Thus, the strength dropped as a result.
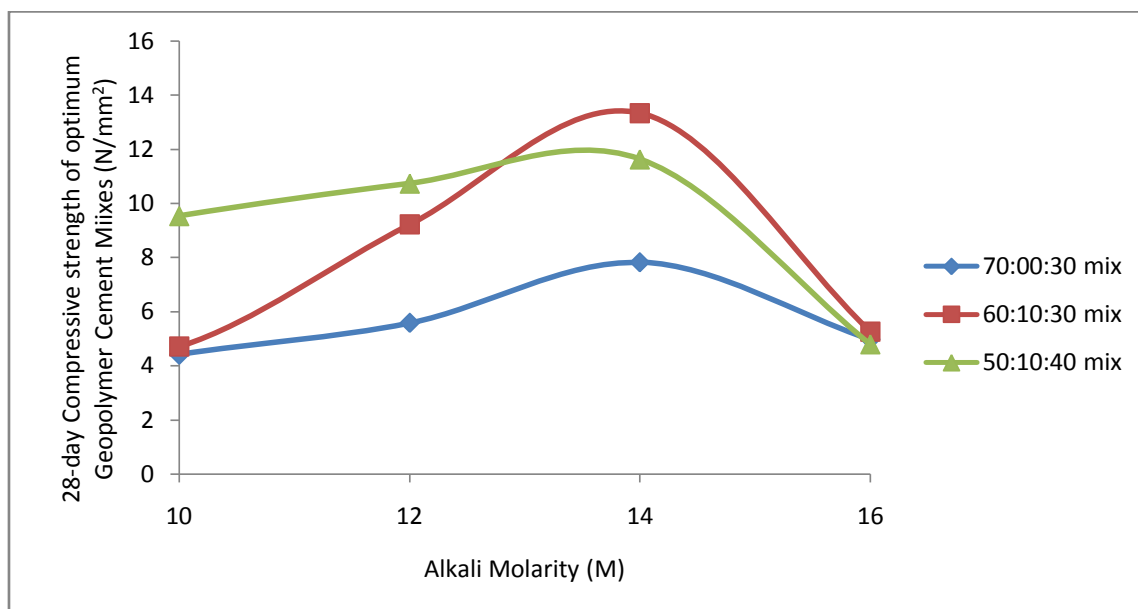

Fig. 5: Variation of optimum 28-day strengths with NaOH molarity for each geopolymer cement group

IV. CONCLUSION

The mass proportioning technique for geopolymer cement mix design was considered as simple for construction practices in that the mass proportioning can be conveniently executed with little or no technical guidance by the construction personnel. Three groups of cement mixes were considered – 70:30, 60:40, and 50:50; with the molarity of the NaOH in the activating medium varying from 10 to 16M in steps of 2M.

Results have shown that three mixes - 70:0:30, 60:10:30, and 50:10:40 cement mixes (CC:NaOH:Na$_2$SiO$_3$) - produced the Calcined Clay Geopolymer Concrete (CCGC) samples with optimum strengths in their respective groups. Moreover, of these three mixes, the compressive strength of concrete samples made with the 50:10:40 mix was the highest, while the 70:0:30 mix had the least strength, up to 12M NaOH. This implies that strengths increase as the level of alkali medium in the cement mix increase. However, as molarity of NaOH rises to 14 and 16M respectively, the overall concentration of the alkali medium is deemed to have reached its optimum effect such that a diminishing effect started occurring. Thus, at 14 and 16M levels, the strengths of CCGC made with the 50:10:40 diminishes; with the 60:10:30 mixes producing the highest strength while the 70:0:30 mix had the least strength of the three mixes. Thus, alkali molarity of about 12M is recommended. Besides, the 60:40 and 50:50 proportional mixes were more desirable.

Though the compressive strengths of the CCGC were generally lower compared to those produced from the traditional Portland cement, they are desirable for low-strength concrete works. This work has presented the beneficial geopolymer cement mix ratios that can be adopted for CCGC samples. The adoption of this technique is deemed convenient for field practice. It is suggested that further investigations should explore the effect of curing at elevated temperature on the strengths of the CCGC samples produced using the technique investigated in this work.

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