EFFECTS OF THE NATURE OF CHEMICAL ACTIVATOR ON THE COMPRESSIVE STRENGTH OF CALCINED CLAY GEOPOLYMER MORTAR

A. S. Bature[a], M. Khorami[b], E. Ganjian[a] and M. Tyrer[a]

[a] Centre for Research in the Built and Natural Environment, Coventry University, CV1 5FB, UK
[b] School of Energy, Construction and Environment, Coventry University, CV1 5FB, UK

ABSTRACT

Low purity kaolin clay is presently receiving attention as a promising aluminosilicate source that has the potential of extending the application of geopolymers because of its global abundance and low embodied energy, but its strength performance depends substantially on the calcination process, mineralogy of the clay, type and proportion of chemical activator etc. This work focuses on comparing the compressive strength of calcined clay geopolymer mortars activated by three forms of chemical activators. Three groups of geopolymer mortar mixes were prepared and tested, group one utilizes sodium hydroxide solution (NaOH) prepared by adding 68% water to the pellets 24 hrs prior to mixing, group two based on sodium silicate solution derived by adding 55.9% water to sodium metasilicate pentahydrate ($Na_2SiO_3.5H_2O$) 24 hrs prior to mixing, while the group three mixes were activated with industry produced Na_2SiO_3 solution that has 54.5% solid component. The results show that high compressive strength is achieved by developing calcined clay geopolymer mortar using high viscosity industry produced sodium silicate solution, while very low strength is achieved by utilizing sodium silicate containing chemically bounded water. The result further shows that the compressive strength of the geopolymer mortars are enhanced by sealed curing of the samples.

Keywords: Calcined clay, sodium silicate, sodium hydroxide, geopolymer, mortar, compressive strength.

1. INTRODUCTION

Alkali Activated Materials (AAM) are receiving significant research attention as materials with lower CO_2 emission and improve strength and durability performance, but most studies focus on utilization of standard compliant Ground Granulated Blast Furnace Slag (GGBS), high purity dehydroxylated kaolin (metakaolin) and Pulverised Fuel Ash (PFA) as precursors (McIntosh *et. al.* 2015). However, almost all the GGBS produced currently is being utilized as Supplementary Cementitious Material (SCM) for Portland cement and is inadequate compared to the demand by the industry, while good quality PFA is increasingly becoming scarce due to continuous decline in production caused by rapid decommissioning of coal thermal power plants that generate the material as a by – product especially in the developed countries, thereby rendering these materials less available for utilization as precursors for large scale geopolymer

application. According to (Scrivener *et. al*. 2016), calcined clay is presently the material with substantial potential to extend the availability of suitable minerals for AAM. Metakaolin produced by calcining high purity kaolin clay has been extensively studied and reported as AAM, but competing demand by different industries for the material, high cost and intensive purification process are some of the factors limiting its availability to be used as either SCM or precursor for alkali activation (Ding 2017). On the other hand, low purity kaolin clays such as lithomarge are cost- effective alternative and offers greater supply sustainability due to availability of vast clay reserves globally supplemented by clay waste generated by the ceramics industries and from construction projects (Fernandez 2009). Clay require some form of processing to enhance its reactivity and calcination is proven to be the most effective treatment, for it to be a suitable precursor for alkali activation (Liew *et. al*. 2016)

The binding phase and reaction product obtained from alkalination of calcined clay is largely dependent on the nature of chemical activator use for the reaction, curing regime, minerology of the clay, etc. Also, appropriate alkali dosage (ratio of Na_2O to precursor) and modulus (ratio of SiO_2: Na_2O) are very critical in the alkalination of calcined clay, if geopolymers are to be achieved. The binding phase of calcined clay geopolymers is almost exclusively aluminosilicate that forms a highly coordinated 3-Dimensional Si-O-Al polymeric network through polycondensation reaction (Provis 2014).

Compressive strength is a basic property of mortar that has very strong correlation with other mechanical and durability properties of paste, mortar and concrete (Deb, *et. al*. 2014). It is against this backdrop that this paper study, compare and report the effects of three forms of chemical activators and their proportion relative to the calcined clay content of the mixes on the compressive strength of calcined clay geopolymer mortars cured under sealed condition and open in the air.

2. MATERIALS AND METHODS

The aluminosilicate precursor used was a calcined clay supplied by Banah UK ltd which was processed by flash calcining low purity kaolin clay obtained from the altered basalt – lithomarge in Northern Ireland and grounded in a ball mill (McIntosh *et. al*. 2015). The calcined clay marketed as banahmeta has 31% reactive silica, specific surface (BET) of 75 m^2g, specific gravity of 2.89 and particle sizes which are 50% (d50) and 90% (d90) finer than 5-8 µm and 16-24 µm respectively. The oxides composition of the calcined clay is presented in table 1.

Table 1: Major oxide compositions (wt. %) of the calcined clay

Oxide (% by weight)	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	MgO	CaO	LOI
Calcined clay	35.18	25.4	29.6	2.9	1.3	0.9	< 2%

The pozzolanic activity of the calcined clay obtained by modified chapelle test is 974 mg CH/g, while its Strength Activity Index (SAI) was determined by comparing the compressive strength of the calcined clay replaced Portland cement mortar mixes relative to the control mortar, and details of these mixes are presented in table 2. All the samples were cured in water bath and tested under surface saturated dry condition for 7, 28 and 56 days. The SAI result is reported as;

$$SAI = A/B * 100 \qquad (eqn\ 1)$$

Where, A is the unconfined compressive strength of the calcined clay replaced mortar specimen (MPa) at 7, 28 and 56 days and B is the unconfined compressive strength of the control mortar (MPa) at the corresponding age.

Table 2: Details of Strength Activity Index (SAI) test mortar mixes

Mortar mixes	Sand: binder	Water: binder[1]	OPC	Calcined clay
100PC	3	0.6	100%	0%
90PC10CC	3	0.6	90%	10%
80PC20CC	3	0.6	80%	20%
70PC30CC	3	0.6	70%	30%

[1]Binder (consist of Portland cement + calcined clay)

Reagent grade NaOH in flakes form of 97% purity and aqueous sodium metasilicate pentahydrate ($Na_2SiO_3.5H_2O$) in mesh granular form obtained from fisher scientific were used as solid components of the chemical activators for the group one and two mixes. The 8 M NaOH solution consist of 68% water, while the sodium silicate solution has 55.9% water content and are prepared 24 hrs prior to their use in the mixes. Also, industry produced high viscosity Na_2SiO_3 solution obtained from Inoxia, UK that contains 45.5% water was used as the chemical activator for the group three mixes. The sharp sand that was used for all the mixes was supplied by local contractor and had particle sizes finer than 4.5 mm and larger than 75 µm sieve sizes. Portable water from the laboratory tap was used as the mixing water.

The description of the details of the geopolymer mortar mixes is given in table 3, while their various proportions are shown in table 4.

Table 3: Description of the calcined clay geopolymer mortar mixes

Group	Sample Label	Activator	Mix variable
1	CC – 32SH	NaOH solution made up of 32% solid	NaOH solution proportion varies from 0.8 to 1.0
	CC – 44.1SSP	$Na_2SiO_3.5H_2O$ solution consisting of 44.1% solid	44.1% $Na_2SiO_3.5H_2O$ varies between 0.8 and 1.0
	SSP:CC =0.7 (ratio of mass of $Na_2SiO_3.5H_2O$ solution to calcined clay)	$Na_2SiO_3.5H_2O$ solution consisting of 58.8% solid	
2	SH:CC = 0.7 (ratio of mass of NaOH solution to calcined clay)	NaOH solution made up of 32% solid	Chemical activator type
	SH:SS = 2.5 (ratio of mass of NaOH to Na_2SiO_3 solutions)	Mixture of NaOH solution made up of 32% solid and high viscosity Na_2SiO_3 solution consisting of 54.5% solid	

3	CC - 54.5SS	High viscosity Na$_2$SiO$_3$ consisting of 54.5% solid	Ratio of mass of calcined clay to Na$_2$SiO$_3$solution

All mortars were designed based on absolute volume method. The mix designed was carried out such that the aggregate to calcined clay mass ratio for group one mixes is 1, while that of groups two and three is 3. The mixing of the 18 calcined clay geopolymer mortar mixes was carried out using a 5 Litre Hobart mixer according to the procedure specified by Kwasny *et. al.* 2018. The mixes were then placed in the 50 mm x 50 mm x 50 mm steel cubes moulds and compacted uniformly using the vibration table. The samples were then covered with polythene bag for 24 hrs before demoulding. Afterwards, the group 2 and 3 samples were sealed cured in a tight plastic box in a conditioning room (20 ± 2 °C and above 65% relative humidity) to limit the effect of carbonation, as well as avoid lost or gain of moisture by the samples, while the samples from group 1 mixes were cured in the air.

Figure 1: Mixing of CC–44.1SSP with L:B of 0.95

Figure 2: The calcined clay geopolymer samples in mould

replicate surface-saturated 50 mm x 50 mm cubes samples was determined at 7 and 28 days as specified by BS EN 12390 – 3:2009, using the JJ Lloyd testing machine that has a loading rate of 10 N/s to accommodate the low strength of most of the samples. Furthermore, microstructure of selected calcined clay geopolymer mortar was probed. The fractured surface of the samples cured at 28 days were vacuum dried and examined by Scan Electron Microscopy (SEM) using Jeol SEM instrument (JSM-6060LV model).

Table 4: Mortar mixes (kg per m^3)

Group 1	Sand	CC – 32SH			CC – 44.1SSP		
L:B		Calcined clay	32% NaOH solution	Free water	Calcined clay	44.1% Na$_2$SiO$_3$.5H$_2$O	Free water
0.8	723	723	579	0	723	579	0
0.85	711	711	604	0	711	604	0
0.9	698	698	628	0	698	628	0
0.95	686	686	652	0	628	652	0
1	675	675	675	0	675	675	0

Group 2	Sand	Calcined clay	32% NaOH solution	58.8% Na$_2$SiO$_3$	Free water
SSP:CC =0.7	1482	484	0	344	64
SH:CC = 0.7	1482	484	344	0	64
SH:SS = 2.5	1482	484	246	98	64

Group 3 (CC - 54.5SS)	Sand	Calcined clay	54.5% Na$_2$SiO$_3$	Free water
0.5	1221	396	198	84
0.75	1482	484	344	64
1	1221	297	297	84
1.25	1221	264	330	84
1.5	1221	238	356	84

3. RESULTS AND DISCUSSION

3.1 Strength Activity Index of the Calcined clay

Figure 2 shows the compressive strength gain as the age increases for the control mortar, as well as the binary mixes, which is as a result of the continuity in hydration reaction of the Portland cement in the mortar cured in water that precipitated the C-S-H gel and Ca(OH)$_2$. For the binary mix mortars, the strength gain indicates pozzolanic reaction between the portlandite and the calcined clay which precipitated additional C-S-H gel but of lower Calcium to Silicate (C: S) ratio. The low strength of the control mortar compared to the binary mixes is thought to be caused by the high water-cement ratio of 0.6, which was use in the mix to accommodate the water demand of the calcined clay for the binary mixes. The 20% calcined clay replaced mix gives the highest compressive strength at 56 days.
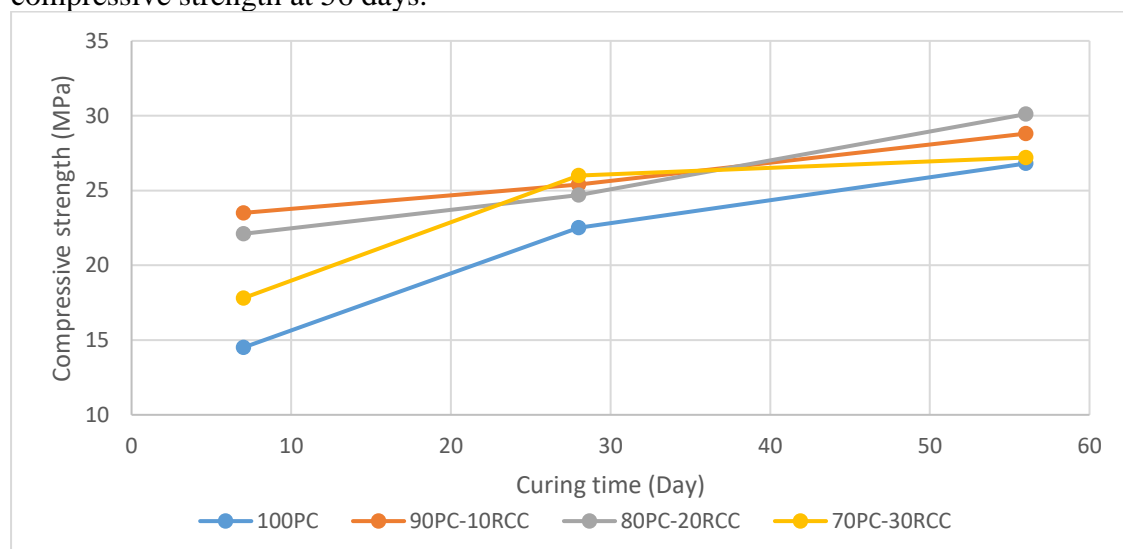

Figure 2: Compressive strength development of calcined clay replaced Portland cement mortars

The SAI of the calcined clay shown in figure 3 for all the mixes is greater than 0.75 indicating considerable pozzolanic activity, as specified by ASTM C618 standard that recommends mortars having 20% pozzolan must achieve strength higher than 75% of the control mortar at both 7 and 28 days. According to Donatello *et. al.* 2009, if the calcined clay was merely a filler in the mix and is inert, there should be a decrease in the compressive strength of the binary mix that correspond to the replacement level of Portland cement in the mix due to dilution effect.
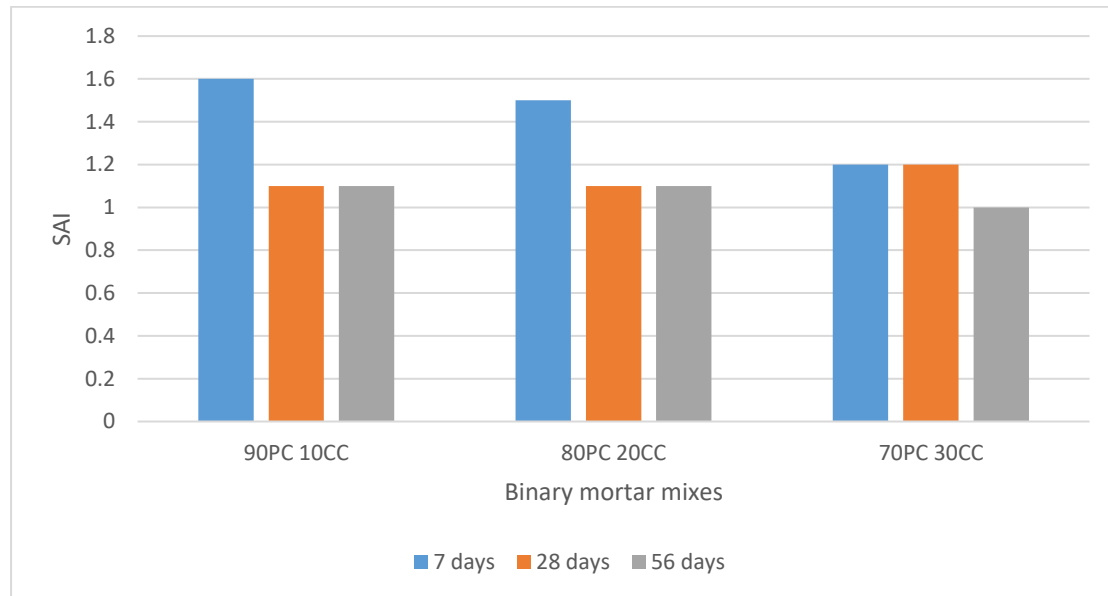
Figure 3: SAI of binary mortar mixes at 7, 28 and 56 days

3.2 Comparing the Strength of Calcined Clay Geopolymer Mortar Activated by Two Forms of Na_2SiO_3 Solutions

The compressive strength of the mortar activated by the high viscosity sodium silicate solution at both 7 and 28 days is much greater than that of the sodium metasilicate pentahydrate dissolved solution as shown in figure 4. Despite the two mixes having the same mass ratio of activator solution to calcined clay, the alkali modulus (ratio of %SiO_2 to Na_2O) varies considerably, which is caused by the variation in the amount of Na_2SiO_3 solid in the two chemical activators. Also, the chemically bounded water in the SSP activator contribute in the dilution of the solution, thereby decreasing its binding effect. This concur with the findings of Bernal *et.al.* 2014 that low strength binder is achieved by activating precursors with hydrated chemical activator. Moreover, for the both mixes which are cured in sealed condition, the strength achieved is low and is thought to be due to the insufficient amount of chemical activator in the mix that will provide the required alkali dosage and modulus.
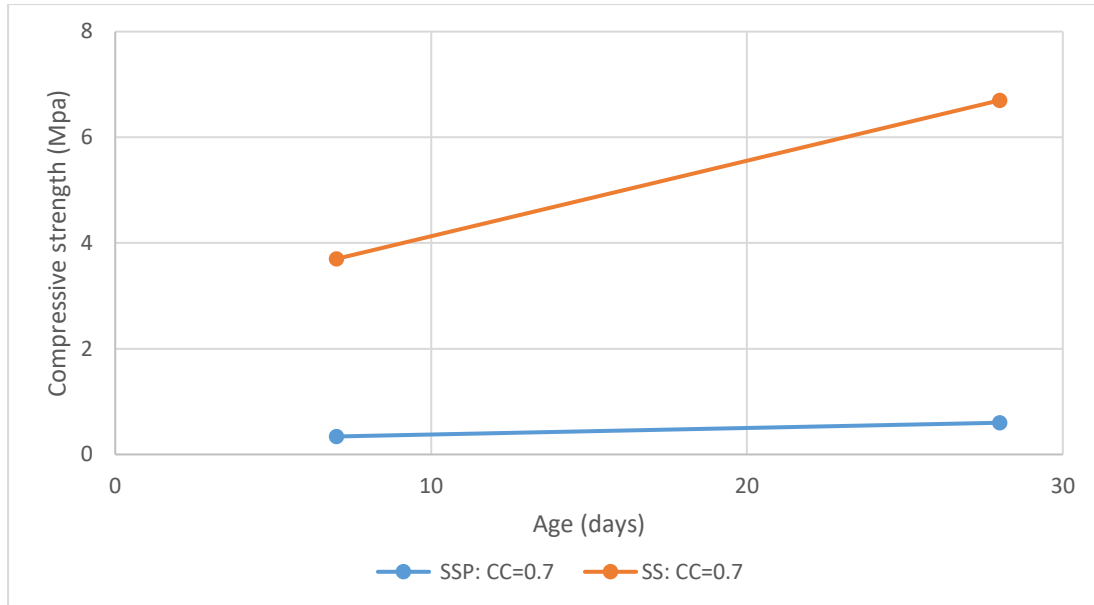
Figure 4: Compressive strength development of calcined clay geopolymer mortars activated by $Na_2SiO_3.5H_2O$ and Na_2SiO_3 solutions

3.3 Effect of Alkali Solution Proportions on the Strength of Calcined Clay Geopolymer Mortar

The result presented in figure 5 shows that significantly higher strength geopolymer mortar is achieved by the alkalination of the calcined clay with 8M NaOH solution compared to the hydrous sodium silicate solution (SSP) regardless of the age and proportion of the solution used in the mixes. The 32% NaOH solution has enhance leaching ability that dissolve the silicate and aluminate in the calcined clay that enrich the binding phase, while the 44.1% $Na_2SiO_3.5H_2O$ solution has reduce binding ability due to the dilution caused by the chemically bounded water.

Moreover, the result of the air cured samples also showed that alkali solution to calcined clay mass ratio of 0.8 gives the highest strength because increasing the amount of chemical activator in the mixes, increases the carbonation attack expressed by equation 2 which results in decreasing the strength of the mortars.

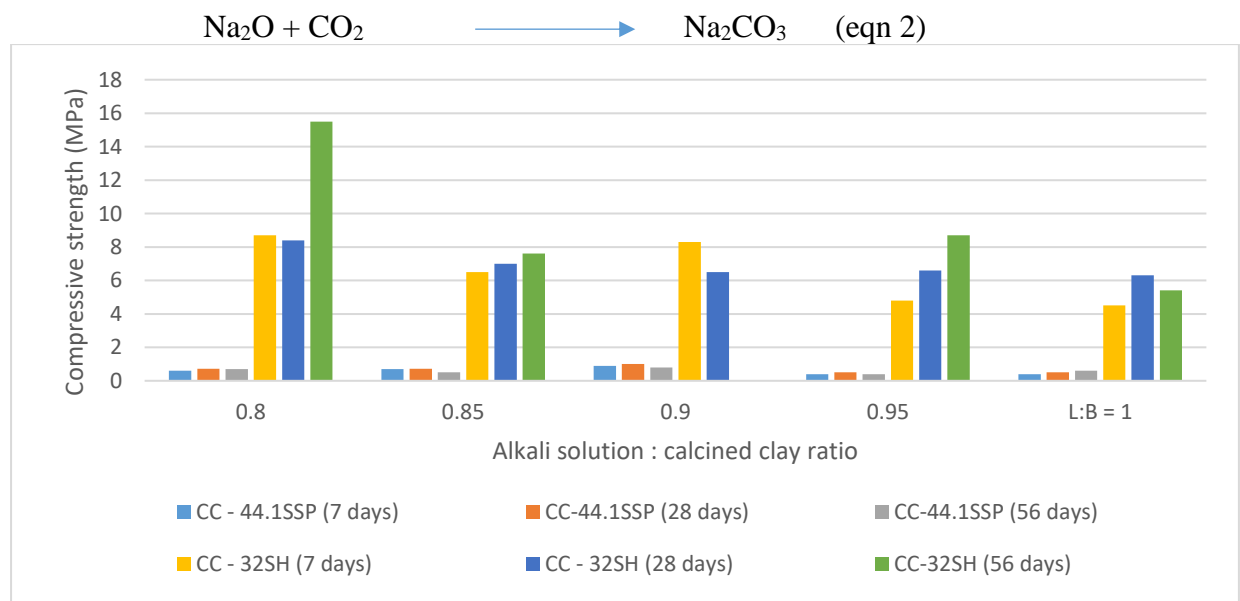$$Na_2O + CO_2 \longrightarrow Na_2CO_3 \quad \text{(eqn 2)}$$

Figure 5: Compressive strength development of calcined clay geopolymer mortars activated by variable proportion of 2 types of chemical activators

For the sealed cured calcined clay geopolymer mortar mixes activated with 54.5% sodium silicate solution, high strength is achieved by using the solution to calcined clay mass ratio within the range of 1 to 1.5 as shown in figure 6. At 7 days, the mortar was a rock mass for the mixes in that mass ratio range and the ratio of 1 gives the highest compressive strength.
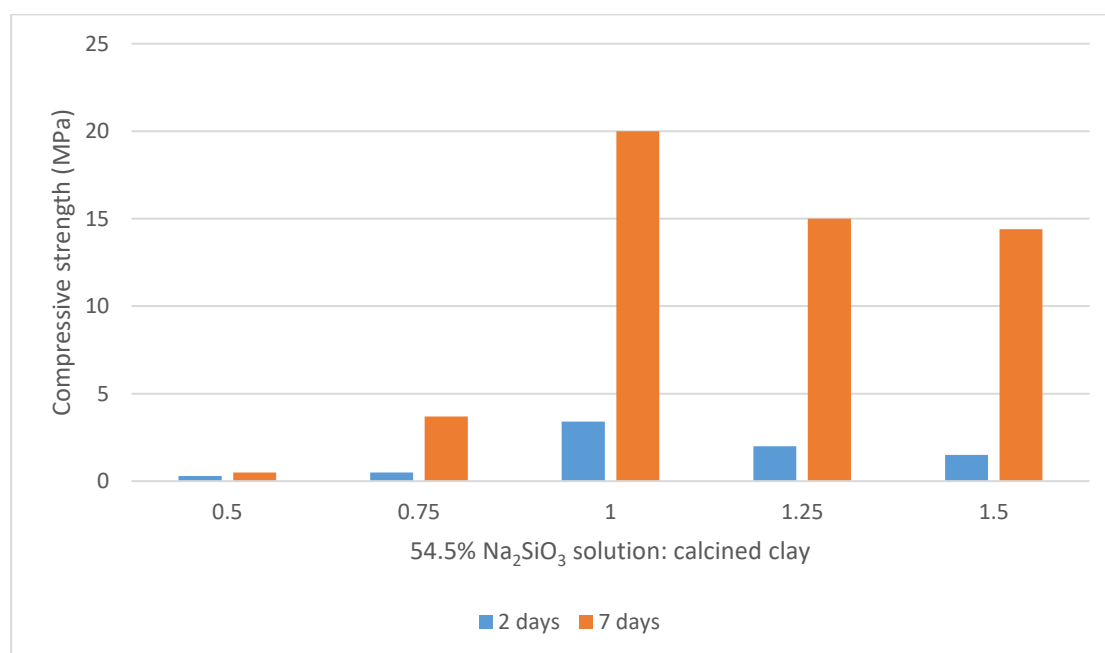

Figure 6: Compressive strength development of calcined clay geopolymer mortar activated by varied proportion of high viscosity sodium silicate solution

Comparing the results presented in figure 4 and 6, a very significant difference in strength is clearly observed between the 54.5% Na_2SiO_3 solution and the hydrous 44.1% $Na_2SiO_3.5H_2O$ solution activated calcined clay geopolymer mortars, in which both were cured under sealed condition. Also, low amount of 54.5% Na_2SiO_3 solution in the mix (i.e 54.5% Na_2SiO_3 solution: calcined clay of 0.5 and 0.75) gives very low strength.

Also, comparing the results presented in figure 5 and 6, it is observed that no meaningful strength was achieved by activating the calcined clay with 44.1% $Na_2SiO_3.5H_2O$ solution and that seal curing enhances the strength of geopolymer mortar compared to air curing by limiting the effects of carbonation.

3.4 Microstructure of the Calcined Clay Geopolymer Mortars Activated by the Three Forms of Alkali Solutions

The microstructure for the CC – 32SH mortar prepared with 8 M NaOH solution to calcined clay mass ratio of 1 cured under sealed condition for 28 days presented in figure 7 reveals a densified and packed structure (a), as well as propagated continuous cracks (b) and pores (c) which may be the cause of the low strength achieved by the mix. The result further shows precipitation of a sponge-like matrix globular unit on the surface resulting from the alkali activation.
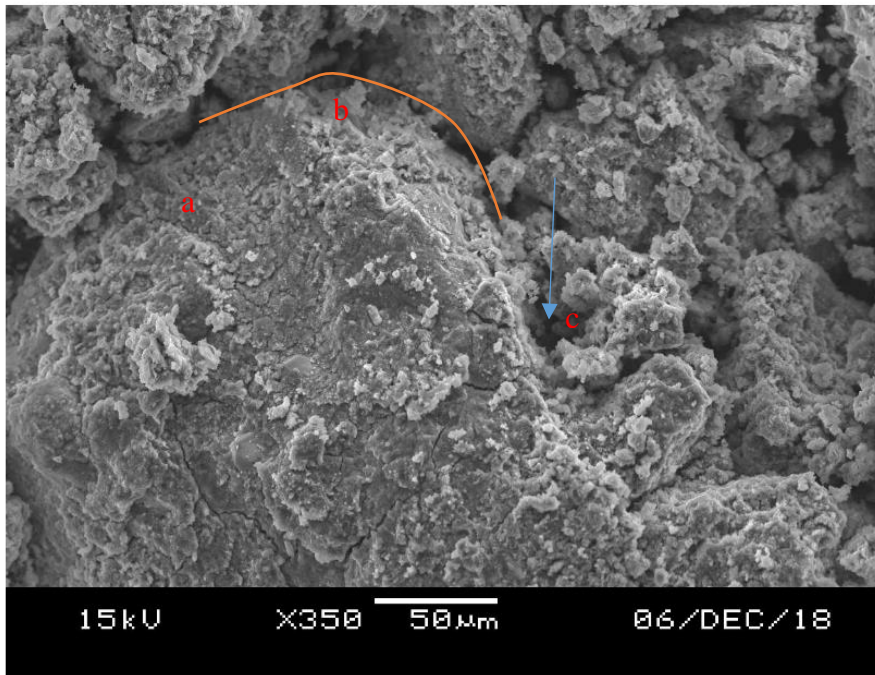
Figure 7: SEM micrograph for CC – 32SH mortar

Figure 8 presents the SEM image obtained for the 28 days sealed cured CC – 44.1SSP mortar which reveals presence of residual particles (a) in the bulk undensified and uncompacted porous structure which is thought to be the cause of the very low strength and density measured for this mix. The heavy presence of the residual unreacted calcined clay particles might have prevented the development of geopolymer network in the mix.
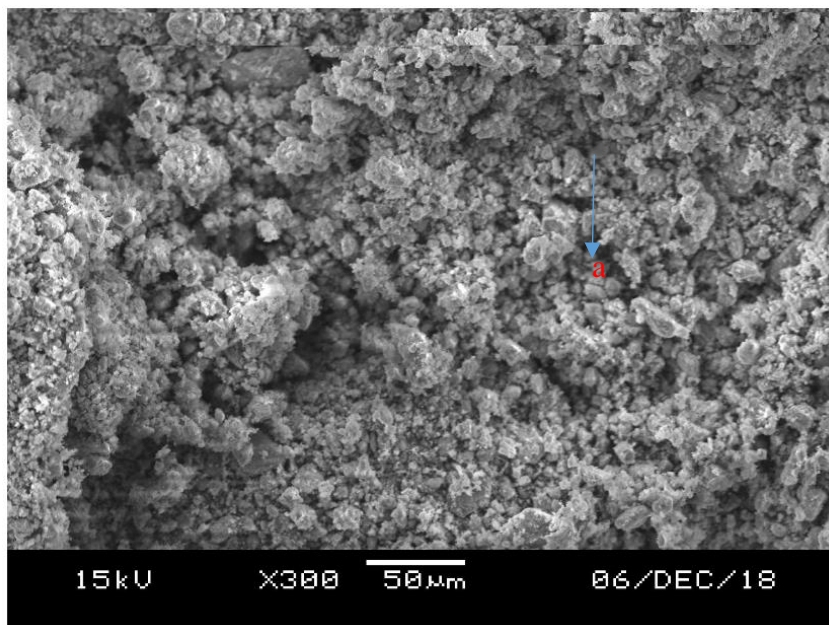

Figure 8: SEM micrograph for CC – 44.1SSP mortar

The microstructure of the CC - 54.5SS mortar prepared with 54.5% Na_2SiO_3 solution to calcined clay mass ratio of 1 cured for 28 days under sealed condition shown in figure 9 reveals a compact rock mass bulk geopolymer structure which resulted in the high

strength mortar achieved for the mix. The SEM image also showed some dispersed cracks which is thought to be caused by the loading of the sample during compression test.
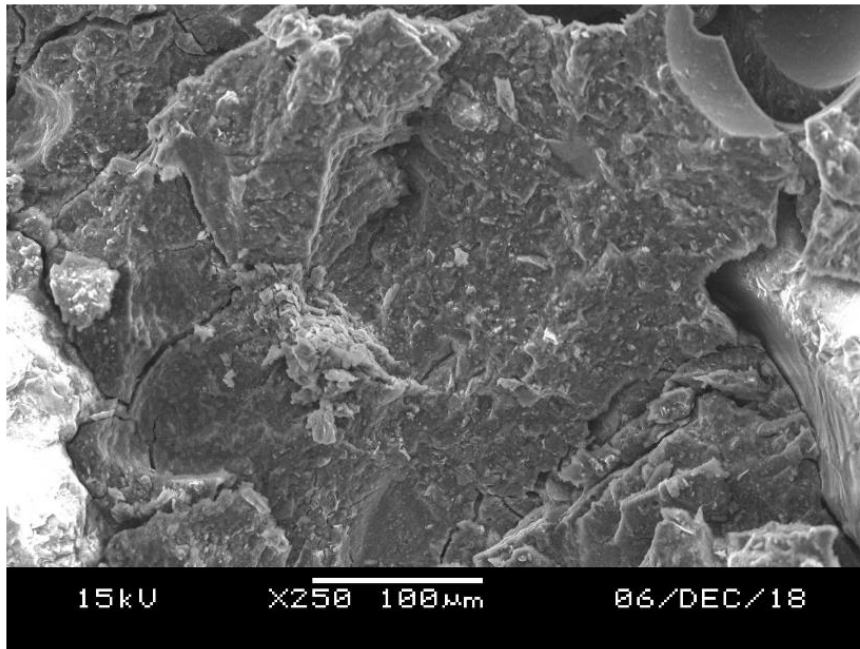

Figure 9: SEM image for CC - 54.5SS mortar

4. CONCLUSION

From the results reported for this experimental study, it can be deduced that, high strength sodium silicate activated calcined clay geopolymers are best obtained using equal mass proportion of the aluminosilicate source and the alkaline solution. The peak strength achieved without any thermal curing lowered the carbon footprint of the calcined clay geopolymer and makes it more convenient for in-situ application. Also, utilizing sodium silicate that contains chemically bounded water (hydrous 44.1% $Na_2SiO_3.5H_2O$) as activator precipitate low strength non-geopolymer matrix that has unreactive residual calcined clay which prevents complete development of geopolymer network. Consequently, the calcined clay may not be suggested to be used as precursor for dry mixing or one-part alkali activation, that are currently been advocated in the literature as one of the strategies that will promote the application of AAM in the construction industry. However, the liquid solution used for the alkalination of the peak strength mortar is a user-friendly activator.

Sealed curing condition is found to enhance the strength of calcined clay based geopolymers by limiting the effects of carbonation, regardless of the proportion or type of chemical activator used.

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