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EFFECT OF SODIUM HYDROXIDE MOLARITY ON THE STRENGTH DEVELOPMNET OF MILLET HUSK ASH - CALCIUM CARBIDE WASTE BINDER BASED-MORTAR

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Abstract

Sodium Hydroxide (NaOH) is an alkaline activator mixed with agro-industrial waste to produce a paste capable of setting and harden within reasonably short period of time. Alarming levels of green gas emission from (PC) Portland cement production and low setting time of millet Husk Ash (MHA) - Calcium Carbide Waste (CCW) products (Mortar and Concrete) has necessitated into utilizing this alkaline activator. MHA - an agricultural waste and CCW - is an industrial waste. Different combination proportions (40:60, 45:55, 50:50) of MHA/CCW were then activated with varied molarities of NaOH solution (5M, 10M, 15M and 20M). The mortar was produced at 1:3 binder / sand (B/S) and 0.5 water / binder (W/B) examined the effect of NaOH for binding, hydration, strength development and water absorption at varied curing age (3, 7, 14, 28 and 56) respectively in accordance to BSEN 196 – 1:2016. The result revealed Alkali-activated Millet Husk Ash-Calcium Carbide Waste (AAMHA-CCW) samples test exhibit increased performance for both properties examined with increased NaOH molarities up to 15M for all combination proportions. At 15M of NaOH (45/55 MHA-CCW) exhibit similar fresh properties (Water demand, setting times and soundness), compressive strength and water absorption as the control (PC) based mortar.

Keywords: Sodium hydroxide (NaOH); Millet husk ash (MHA); Calcium carbide waste (CCW); Alkali-activated binder; Alkali-activated Millet Husk Ash-Calcium Carbide Waste (AAMHA-CCW).

INTRODUCTION

Cement is a common building material used as a binder in construction industry. Nonetheless, the production of cement leads to carbon dioxide (CO^2) emission especially during clinker production as reported by Olawuyi *et al. (*2017)

$$CaCO_3 \xrightarrow{heat\ (>900\ C)} CaO + CO_2 \qquad (1.1)$$

The most important constituent of a PC are calcium oxide (CaO), silica (SiO_2), alumina (Al_2O_3) and ferric (Fe_2O_3) with strength determinant being the SiO_2 which combined with CaO in the presence of water to form hydrated lime – $Ca(OH)_2$. This reaction leads to the formation of calcium silicate hydrate – CaO-SiO_2-H_2O (C – S – H), the final product of strength development in cement hydration process after water contact (Olawuyi *et al.* 2017).

$$CO_2 + SiO_2, + Al_2O_3 + Fe_2O_3 \xrightarrow{heat\ (>1450\ ^{o}C)} CaO, SiO_2, Al_2O_3 \ \&\ Fe_2O_3 \qquad (1.2)$$

Therefore, PC exhibit similar reactive properties as of those pozzolanic materials. Pozzolans are fine materials that contain silica and alumina which on their own have little or no binding property but when combined with lime in the presence of water, will set and hardened like cement (Abdulfatai *et al*, 2013). Hence, to curtails the problem associated with atmospheric gas emission during PC production, there is urgent needs of producing eco-friendly binder (MHA, CCW (Onuche *el al,* 2019); volcanic ash (Hassan, 2006); Corn-cob ash [CCA] (Raheem, 2010), millet husk ash [MHA] (Anowai and Jones, 2015 and NaOH activation as a fast set enhancer (Olonade and Bello (2018); Qureshi and Ghoshi, (2013).The (Portland- pozzolan) cement reactions are shown in equation (1.2) and (1.3) as follows:

$C_3S + H \rightarrow C - S - H + CH$ (1.3)

Pozzolan + CH + H → C-S-H (1.4)

Where C = CaO, S = SiO_2 and H = $(OH)^-$

The reaction in equation (1.3) is known to be fast and lime producing while the reaction in equation (1.4) is rather slow or latent depending on the properties of the pozzolanic material.

According Martinez and Palomo (2001), Alkali activation (NaOH) is the chemical process where an amorphous structure is transformed into a skeletal structure that exhibits cementitious properties. The material containing reactive silica or alumina can be activated as shown in equation (1.5) and (1.6).

$Na(OH)_2 + SiO_2 \rightarrow$ N-S-H (Gel) as in geopolymer (1.5)

$Na(OH)_2 + Al_3O_2 \rightarrow$ N-S-H (Gel) as in geopolymer (1.6)

Where N-S-H (Gel) is Sodium-Silicate-Hydrate Gel.

Bakharev (2006) reported that concrete produced using alkali-activated fly ash with NaOH achieved a two-day compressive strength of 10 N/mm^2 while the 28days compressive strength was 60 N/mm^2. The materials that rich in alumina and silicates such as fly ash, kaolinite and slag can be used in geopolymer as mineral sources. The reactivity of these sources depends on the chemical composition, particularly the content of silica oxide (SiO^2), alumina oxide ($Al2O^3$) and calcium oxide (CaO), the morphology of the particle shapes, phase of materials as well as the particle sizes. According to De Vargas, A. S. *et al.,* 2011; Bing-hui, H. M. *et al.,* 2014 geo-polymerization process can be referred as alkaline activation where it transforms the amorphous phase of source materials into composite which have binding property. The presence of strong alkaline solution such as sodium hydroxide (NaOH), potassium hydroxide (KOH), water glass or their combinations are required for geo-polymerization to occur. The activation of fly ash and other pozzolans with alkaline solution dissolves the soluble amorphous phase during geo-polymerization and form geopolymer product. The product from geo-polymerization process was an amorphous to semi-crystalline 3-Dimensional aluminosilicate framework structures with a combination of silica $[SiO_4]$ 4- and alumina [AlO4] 5- tetrahedral (Somna, K., 2011).

RESEARCH SIGNIFICANCE

The need for developing alternative binder cannot be undermined in the presence of changing economic realities (skyrocketed prize of cement and other building materials) and the quest for sustainable eco-system. The challenge is not just to source alternative cementitious materials but a great deal of research is required to solve major, significant processing, reactivity and early setting time issue with the view to establishing good performance level in concrete /mortar produced from such binder.

EXPERIMENTAL PROCEDURE

Materials

This research work was carried out with these materials: MHA, CCW, NaOH, (PC) CEM II 42.5N (Dangote 3X cement) and fine aggregate. The MHA was sourced from Garatu village near Minna) in Bosso Local Government Area of Niger State, Nigeria. The husk was incinerated in an open-air with locally fabricated incinerator presented earlier in Abalaka (2013). This material was ground to finer particles at Central Services Laboratory of National Cereals Research Institute (NCRI), Badeggi, near Bida, Niger State and sieved with a 75 µm sieve and the particles passing used as the MHA –SiO_2 sources for the study. CCW– an industrial waste of acetylene gas production was collected from the disposal area of a local automobile Welder's ("Panel Beater's") workshop in the mechanic village of Keteren-Gwari, Minna, Niger State. It was sun-dried for a day and calcinated in a furnace at a temperature of 700^{o} C to obtain its amorphous form and was used as the CaO source. The NaOH used was purchased from Panlac Chemical Laboratory, Minna.

Methods

The study involved the determination of the physical and chemical properties of the constituent materials for mortars for proper characterization as reported Onuche et al. (2019). The effect of the varied NaOH concentrations **on** binder**s** were examined on the strength development and water absorption of the different proportion combination MHA-CCW based mortar samples at requisite curing ages of 3, 7, 14, 28 and 56 days while PC based mortar samples of 1:3 (C/S) at 0.5 water/cement ratio (W/C) prescribed in BS EN 196-1:2016 served as control.

Physical and chemical properties

Particle size distribution test was conducted on the natural sand using the dry-sieve approach in accordance to BS EN 196-1: 2016 for proper classification of the sand sample. The particles passing the 1.18mm sieve but retained on the 75µm sieve was used for the study. The 75µm sieve was used as the limit value for sand used as reported Onuche et al. (2019). X-Ray fluorescence (XRF) analysis for the oxide composition was conducted on the cementitious materials (MHA, CCW and PC) at National Geoscience Research Laboratory, Kaduna, Kaduna State, using XRF Analyser

Setting time and soundness of cement and agro-industrial binders

The initial and final setting times and Le-Chatelier soundness tests for the proportion combinations of MHA/CCW with different molarities of NaOH (5, 10, 15, 20M) and PC were determined using neat pastes of standard consistency in accordance with BS EN 196-3: 2011. Vicat apparatus model No EL 38-2010 by ELE was used for measurement of the consistency.

Determination of Mixing Proportion of MHA and CCW

The suitable mix proportions of MHA and CCW was determined adopting the molar ratio concept taking cognizance of the SiO_2 and CaO contents of MHA and CCW respectively to arrive at 40:60; 45:55; 50:50 of MHA-CCW combination proportions. For the control mortar mix, PC was used at 1:3 C/S at 0.5 W/C. NaOH at different concentrations of 5, 10, 15, 20M was prepared for the study. The choice of NaOH concentrations was based on the findings from the Olonade and Bello, (2018) and Ammar *et al.,*).

Determination of Compressive Strength of Mortar Sample

The compressive strength is a key property of mortar to which numerous of its characteristic are related (Neville, 2012). 50 mm cube mortar samples were cast and cured by water immersion for the requisite ages (3, 7, 14, 28 and 56 days) before testing for compressive strength. The mortar cubes were removed from the curing tank and put in the open air in the laboratory to surface dry, weighed and placed at the centre of hydraulic Digital Universal Testing Machine (DUTM - 20) for crushing force (P) determination in consonance with BS EN 196-1 (2016). The compressive strength was calculated using equation (3.1).

$$CS = \frac{P}{A} \tag{3.1}$$

Where;

CS = compressive strength in N/mm^2; P = maximum load at failure in N (Newton) and A = cross-sectional area, in mm^2.

Determination of Water Absorption of Mortar Sample

The water absorption test involved removing the mortar cubes were removed from the curing tank and allowed to surface-dry before placed in the electric oven to the oven-dry at 105 ^oC for 72 hours. The oven was then switched off, allowed to cool back to room temperature before removing the test samples and weight measurements taken and recorded as initial weight (w_1). The final weights were determined after immersing the mortar samples in the curing medium for 30 minutes, removed, towel-dried, re-weighed again and the value was recorded as (w_2). The water absorption of the mortar samples was then calculated using equation (2.2) under BS 1881-122, (2011)

$$Water\ Absorption = \frac{(w1 - W2) * 100}{w1} \tag{3.2}$$

RESULTS AND DISCUSSION

Chemical Analysis of the Cementitious Materials

From table 1 as presented in Onuche et al. (2019), the main component of MHA is SiO_2 (74.2 %). MHA is thus classified as a class F Pozzolan since the summation of the main oxides (SiO_2 + Al_2O + Fe_2O_3) gives 88.1% which is above 70 % minimum limit stipulated in ASTM C618 (2015) standard. Also, SO_3 is below 4% and Loss on Ignition (LOI) is less than 10% conforming to the codes specification. The CCW was observed to contain 66.1 % CaO similar values to the CaO content (65.0 %) of the PC and lower SiO_2 and Al_2O_3. The LOI of 28.2 % of CCW was observed to be above the specified 10% maximum and similar to that of PC as reported by Manesseh & Joseph (2016) of 32.51%.

Table 1: XRF Analysis for Oxide Composition of Cementitious Materials

MHA	72.4	14.2	2.0	1.5	1.0	6.4	0.2	0.0	0.5	0.0	0.0	0.2	0.1	0.1	88.1
CCW	5.5	1.8	28.2	0.3	0.1	66.1	0.1	0.1	0.0	0.0	0.0	0.0	0.1	0.2	7.6
CEMI	21.3	5.1	0.0	1.1	2.8	65.0	0.0	0.1	0.0	4.4	0.0	3.5	0.0	4.5	27.5

Fresh and Early Strength Properties

The summary of water demand, setting times and soundness of the binders (i.e. PC and MHA: CCW) pastes with different molarities of NaOH contents as presented in Onuche et al. (2019) are shown in Table 2. This reveals that the PC recorded the least standard consistency of 28.3%, this were as a result of rapid hydration of C-S-H as affirmed by Olawuyi *et al.* 2017 and that of AAMHA/CCW increased progressively from 46.6% to 31.5% (0M -15M) and at 15M has similar properties to the control (PC) of mix proportions 45:55 MHA/CCW.

Setting Times of Binder Pastes

Table 2, it was observed that there are progressive decrease in both initial and final setting time of Pozzolan cements as the molarities of NaOH increased from 5 to 15M, similar effects were reported by Martinez & Palomo, (2001) but experienced a sharp decreased at 20M across all mix proportions.

For 40:60 (MHA: CCW) mix proportion, the initial and final setting of the Pozzolan cement paste was recorded as 305 and 207 minutes as compare to control (PC based mortar). As the NaOH molarities increased for the Pozzolan cement paste, there exists progressive decrease in both the initial and final setting as shown in Table 2. The 40:60 (MHA: CCW) at 15M NaOH molarity possessed fresh properties similar control (PC based mortar).

For 45:55 (MHA: CCW) mix proportion, the initial and final setting was noted to be 270 and 305 minutes as compare to PC based-mortar (28.3 and 95 minutes). As the NaOH molarities increased, there was a progressive decrease in both the initial and final setting as shown in Table 2. The specimen at 15M NaOH molarity revealed similar fresh properties to that of PC based-mortar.

For 50: 50 MHA/CCW mix proportion, there was a progressive decreased in both the initial and final setting time as the activator dosage increased from 5 to 15M as showed in other mix proportions above.

Optimum mix composition for acceptable setting time of the alkali-activated MHA: CCW is adjudged to be 45: 55 (MHA: CCW) activated with at 15M of NaOH since it possessed fresh properties closest to that of the PC based mortar.

Table 2: Summary of Water demand, setting times and soundness test of the Binders

Specimen No	Binder Type	Water Demand (%)	Penetration (mm)	Soundness Expansion (mm)	Initia Setting Time (mins.)	Final Setting Time (mins)
PC	CEM 1	28.3	5.0	0.0	60	95
40/60	0 M	56.6	6.0	0.5	305	270
	5 M	56.6	5.5	0.0	135	210
	10 M	56.6	5.5	0.0	105	150
	15 M	63.3	5.0	1.0	90	110
	20 M	63.3	5.0	0.5	105	120
45/55	0 M	46.6	5.5	0.5	270	305
	5 M	40.2	6.0	0.0	120	152
	10 M	36.3	5.5	0.5	90	120
	15 M	31.5	5.0	1.5	75	100

	20 M	35.4	5.5	1.0	90	135
50/50	0 M	44.6	5.5	0.5	240	375
	5 M	42.6	6.0	0.0	150	195
	10 M	42.0	5.5	0.5	120	145
	15 M	40.0	5.0	1.5	90	115
	20 M	45.0	5.5	1.0	105	135

Influence of NaOH contents on Compressive Strength

Figure 1 reveals the influence of NaOH molarities on the compressive strength of the AAMHA-CCW binder based-mortar. The compressive strength generally increased as the NaOH molarity increases up to the 15M NaOH concentration. This is attributed to the conversion of the $Na(OH)_2$ crystals into the secondary N-S-H gel. This showed that the peak of hydration of Silica, Alumina of MHA and CaO of CCW with NaOH was attained at 15M. The NaOH molarity effect on the mean compressive strength further affirms the 15M NaOH as the optimum concentration of NaOH for best performance in strength for the NaOH activated MHA-CCW binder based mortar. Same effects were observed and reported by Zarina *et al.* (2017); Qureshi, & Ghoshi (2013); Martinez & Palomo, (2001).

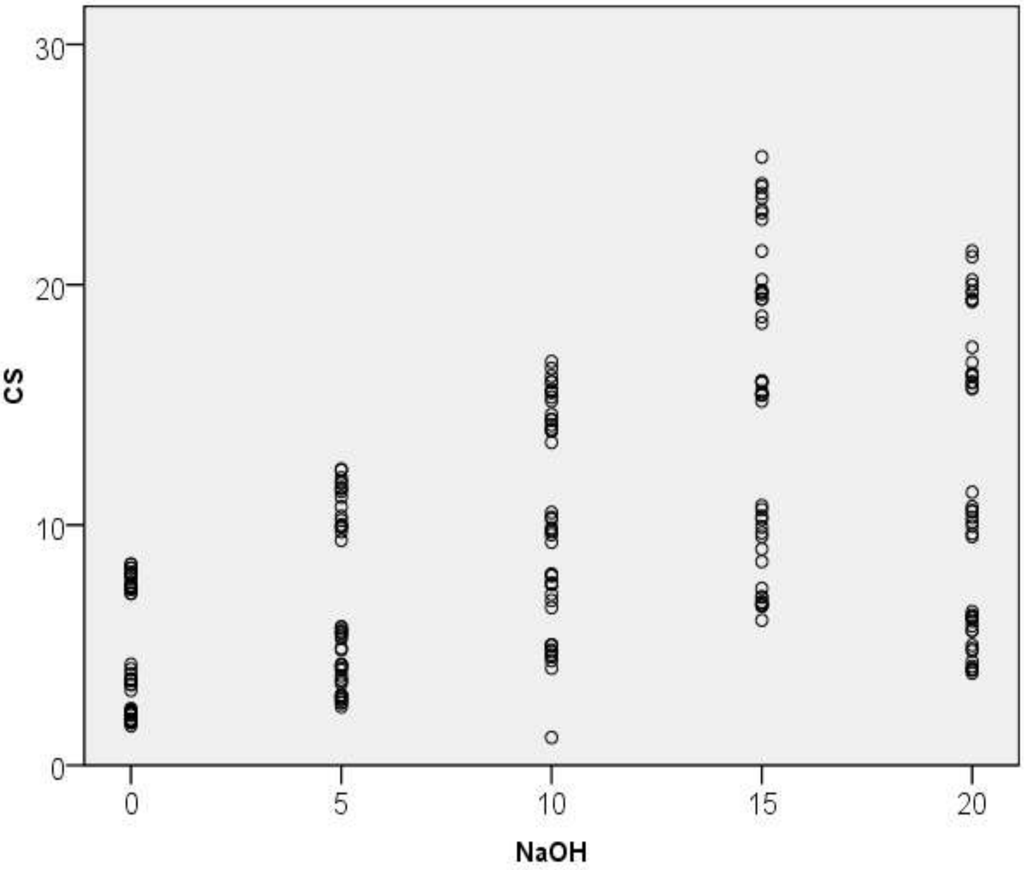

Figure 1: Influence of NaOH contents on Compressive Strength

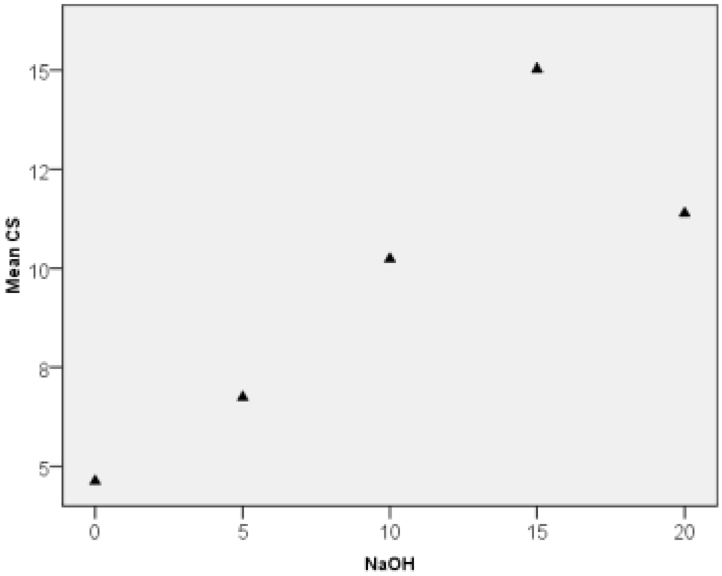

Figure 2: Influence of NaOH Molarity on Mean Compressive Strength Values

Influence of the NaOH molarity on the mean water absorption of the AAMHA-CCW binder based mortar also affirmed the 15M NaOH as the optimum concentration of the mortar for best performance in the durability property examined. Similar tread was noticed in Zarina *et al.* (2017); this occurred as a result of total breaking down of bond between C-S-H and N-S-H (Gel) of AAMHA-CCW.

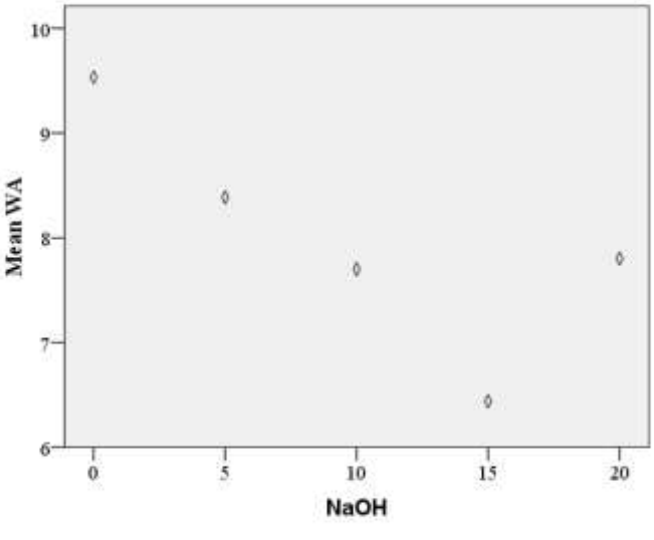

Figure 3: Influence of NaOH Molarity on Mean Water Absorption Values

Influence of MHA, CCW, NaOH molarity and Curing age (called independent variables) were examined on the compressive strength and water absorption (dependent variables) of the alkali-activated MHA-CCW binder based mortar using statistics (general linear model - multivariate) as shown table 3. This is to examine which of the independent variables had significant effect on compressive strength and water absorption of the mortar. The statistical analysis indicated that all the independent factors when considered individually had significant effect on both the properties examined at 95 % confidence level ($\alpha = 0.05$) as a result of the presences CaO, SiO_2, Al_2O_3 & Fe_2O_3 and NaOH which produced C-S-H and N-S-H (Gel). The test between-subject effects also reveal significant effects except combined effect of NaOH and curing ages (as highlighted) at the two factor analysis level which is not significant. This implies that whenever any of the factors (MHA, CCW, NaOH molarity, and curing age) vary, the compressive strength and water absorption also changes. The degree of variation is proportional to the magnitude of the change. The coefficient of determination (adjusted R-Square value) obtained from the analysis was 0.992 (99.2 %). This suggests strong statistical association between each independent variable and the dependent variables. This is evident based on the current research trend (Olonade and Bello, (2018) and Ammar *et al.,* 2013 Zarina *et al.* (2017).

Table 3: Tests of Between-Subjects Effects

Source	Dependent Variable	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	CS*	3233.150[a]	31	104.295	399.624	.000
	WA*	368.081[b]	31	11.874	57.756	.000
Intercept	CS	22159.182	1	22159.182	8.491E4	.000
	WA	4064.914	1	4064.914	1.977E4	.000
NaOH	CS	2170.132	4	542.533	2.079E3	.000
	WA	209.853	4	52.463	255.193	.000
CAges***	CS	98.210	1	98.210	376.306	.000
	WA	33.489	1	33.489	162.897	.000
NaOH * Cages	CS	38.714	4	9.678	37.084	.000
	WA	3.253	4	.813	3.956	.006
Error	CS	16.703	64	.261		
	WA	13.157	64	.206		
Total	CS	26130.698	96			
	WA	6632.744	96			
Corrected Total	CS	3249.853	95			
	WA	381.238	95			
a. R Squared = .995 (Adjusted R Squared = .992)						
b. R Squared = .965 (Adjusted R Squared = .949)						

*CS = Compressive Strength; WA = Water Absorption; CAges = Curing Ages; df = degrees of freedom, F = F-ratio, Sig. = exact significance level.

CONCLUSION AND RECOMMENDATIONS

In this study, agro – industrial waste materials (MHA and CCW) were activated at varied molarities of NaOH for performance assessment at utilization as alternative binder in mortar as compared to PC based mortar. The chemical analysis revealed MHA has total $SiO_2 + Al_2O_3 + Fe_2O_3$ above 70% and can be classified as a Class N Pozzolan while CCW is a good CaO source. The compressive strength results of AAMHA-CCW increases up to 15M and slightly decreases at 20M as the percentage mix of NaOH molarity increases. At 15M NaOH (45: 55 MHA/CCW), showed the best combination proportions and of similar characteristics as the PC based mortar at 56 days of curing. Based on the finding of this study, hereby recommended the following:

i. Further studies on the influence of temperature slightly above the ambient temperature on the hydration rate and strength development of MHA/CCW binder at varied NaOH molarities.
ii. Future studies on the product of hydration should be conducted using scanning electron microscopy (SEM) and X- ray diffraction (XRD) analyses.
iii. There were potential that the AAMHA-CCW could be further explored using different optimization approach to produce higher strength for structural use, like normal strength mortar.

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