Chemical and Physical Characteristics of Blended Cements Produced from Softwood Ash

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Abstract

In an attempt to convert agricultural residue to alternative binding material for use in construction industry, this research considered the use of wood ash from Anacardium- occidentale (kaju) wood which is softwood as a pozzolan in cement production. In this study, the chemical composition (silica (SiO₂), aluminum oxide (Al₂O₃), ferric oxide (Fe₂O₃), calcium oxide (CaO), magnesium oxide (MgO), sulphur trioxide (SO₃), sodium oxide (Na₂O) and potassium Oxide (K₂O)) of the ashes and the clinker was investigated. The production of blended cements were carried out in the factory by replacing 5- 50% by weight of Ordinary Portland Cement Clinker with the ashes during the manufacturing process. The cement without wood ash serves as the control. The physical characteristic (fineness, initial and final setting times, heat of hydration and residue on 45µm sieve), and the chemical composition of the blended cements were also investigated. The results showed that Anacardium-occidentale ash (AOA) was a suitable material for use as pozzolan since it satisfied the requirement for such a material by having a combined SiO₂, Fe₂O₃ and Al₂O₃ of more than 70% according to ASTM C 618. The AOA blended cements satisfied standard requirements for up to 20% replacement level. It was concluded that the wood ash was suitable for use in the production of blended cements.

Keywords: Anacardium- occidentale ash (AOA), Wood Ash (WA), Pozzolan and Blended cement.

Introduction

Other ingredients in concrete apart from cement which is the only factory made standard component are water and aggregates which are natural materials. Cement is a finely ground, non-metallic, inorganic powder which when mixed with water forms a paste that sets and hardens. This hydraulic hardening is primarily due to the formation of calcium silicate hydrates as a result of the reaction between mixing water and the constituents of the cement (Cement Association of Canada, 2001). Cement is a powdery material made of clinker, gypsum and other additives. It is mainly used to form concrete which is widely used for civil engineering constructions. Cement production is expected to increase from 3.27 billion metric tons in 2010 to 4.83 billion metric tons by the 2030. This increasing demand for cement is expected to be met by partial cement replacement (Coutinho, 2003). The search for alternative binder or cement replacement materials led to the discovery of the potentials of using agricultural residue as cementitious materials.

Agricultural residue use in cement production is an environmental friendly way of disposing large quantities of materials that would otherwise pollute land, water and air. Some agricultural residues which possess pozzolanic properties and have been studied for use in blended cement are Rice Husk Ash (Chungsangunsit *et al.*, 2007, Coutinho, 2003), Bamboo Leaf Ash (Dwiveldi *et al.*, 2006), Palm Fruit Ash (Olunode, 2010), Locust Bean Pod Ash (Adama and Jimoh, 2011), Cement Cassava Peel Ash (Salau *et al.*, 2012), Corn Husk Ash (Raheem *et al.*, 2012), Corn Cob Ash (Adesanya and Raheem, 2009, 2010) and wood ash (Raheem and Adenuga 2013, Abdullahi, 2006 and Etiegni and Campbell, 1991).

Wood ash could be used as a pozzolan in concrete and mortar (Abdullahi, 2006) since it is obtained from the combustion of wood. It can also be related to fly ash since fly ash is obtained from coal, which is a fossilized wood. Significant quantities of wood ash are currently being produced near the industries that use wood as a fuel partially or fully and this poses a threat to the environment. The possibility of adding wood ash to cement for concrete production was explored by Abdullahi (2006), in which wood ash was used as an admixture in the study. Marthong (2012) analysed the hydration characteristics of saw dust ash admixture cement and concluded that 10% addition of wood ash to cement is optimum. High calcium wood ash and densified silica fume blended cement paste was characterized by CheahChee and Mahudin (2011). Chemical analysis of wood ash showed that it has pozzolanic properties (Etiegni and Campbell, 1991). Raheem and Adenuga (2013) studied wood ash from bread bakery as partial replacement for cement in concrete and concluded that a maximum of 10% wood ash substitution is adequate for use in structural concrete. Raheem and Orogbade (2018) studied the characteristics of blended cements produced from hardwood ash and concluded that up to 20% replacement level of all the wood ashes were suitable for use in the production of blended cements.

Previous studies showed that many researchers such as Raheem and Adenuga (2013) have worked on the mixture of wood ash and ordinary Portland cement at the point of need, without considering the type of wood (either from softwood or hardwood) and without considering blending of wood ash with clinker and gypsum during factory production of the cement except for Raheem and Orogade (2018) who studied some hardwood only. Therefore, this study focused on determination of chemical composition of wood ashes from softwood, as well as the physical and chemical properties of the blended cements produced at varying percentage replacement of each wood ash during the manufacturing process.

Materials and methods

Materials

The softwood that was used to produce the wood ash is *Anacardium- occidentale* (kaju), the wood was burnt in a bread bakery that uses wood as fuel for their operation and the ash was collected using clean sacks. The wood ash was sieved and only those retained on a 0.425µm sieve was used for the study. The ash was taken to Larfarge Cement, West Africa Portland Cement Company (WAPCO) Sagamu, Ogun State, Nigeria, for chemical analysis. The analyses of the ash was carried out using X-ray Fluorescence analyser (Model QX 1279). The clinker used to produce the blended cement was obtained from Larfarge Cement, WAPCO Sagamu, Ogun State, Nigeria, which is the clinker used by the company to produce Ordinary Portland Cement (OPC) and the chemical analysis was also carried out.

Cement mixtures

The milling involved the replacement of 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45% and 50% by weight of Ordinary Portland Cement Clinker with the ash during the manufacturing process. Ten (10) series of *Anacardium- occidentale* ash (AOA), were prepared for cement milling. Ordinary Portland Cement (OPC) without ash content served as the control. As it is the practice in WAPCO Sagamu works, 5% gypsum was used for the cement milling. The milling machine used is a Laboratory Ball Mill (Model R. PM 1400/50, Serial Number 93021.A). The mill was charged with media balls following the order and distribution given below:

90 mm	-	8.2 kg
80 mm	-	10.0 kg
60 mm	-	10.0 kg
50 mm	-	4.0 kg
30 - 40 mm	-	12.8 kg

The ball mill was charged with the required weight of clinker, AOA and gypsum. After which it was firmly tightened and put in operation for 55 minutes. The specific surface area (SSA) of the cement midstream is tested to ensure that it is not less than 250 mm²/kg in line with NIS 439:2000 requirement. The milling was done in batches of 4 kg. Table 1 shows the mix proportion for each batch and the percentage ash replacement.

Table 1: Mix proportion for changing ball mill

Percentage of Ash replacement (%)	Percentage of Clinker (%)	Weight of Clinker (g)	Weight of Ash (g)	Weight of Gypsum (g)
0	95	3800	-	200
5	90	3600	200	200
10	85	3400	400	200
15	80	3200	600	200
20	75	3000	800	200
25	70	2800	1000	200
30	65	2600	1200	200
35	60	2400	1400	200
40	55	2200	1600	200
45	50	2000	1800	200
50	45	1800	2000	200

Note:

- (i) Gypsum is 5% of the total weight throughout.
- (ii) Total weight charged per batch was 4000 g.

Testing of blended cements

The following physical characteristics of each of the softwood blended cements produced were determined:-

Fineness: - The fineness of the blended cements produced were determined using air permeability method (Blaine method) as specified in BS EN 196-5: 1995. The equipment used was the weighing balance and the blaine permeability.

Residue on 45µm sieve: - The residue on 45µm sieve was determined as specified in BS EN 196-5: 1995. The equipments used were weighing balance, 45 µm Sieve and sieving machine.

Initial and final setting times: - For the determination of the initial setting time, a round needle with a diameter of 1.13 ± 0.05 mm was used. A similar needle fitted with a metal attachment 5 mm in diameter was used to determined final setting time.

Heat of hydration: - Heat of hydration of the blended cement was determined by heat of solution method using vacuum flask calorimeter fitted with a Beckmann thermometer as specified in ASTM C 186-82: 1995. Mixture of dry cement, nitric and hydrofluoric acid was placed inside the flask and the temperature rise was measured in degree Celsius on the thermometer after six (6) hours.

Also the chemical characteristics of each of the blended cements were determined using X-ray fluorescence analyser (Model: QX 1279) as specified in BS EN 196-2: 1995 adopted. The chemical compositions that were determined are silica (SiO_2), aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3), calcium oxide (CaO), magnesium oxide (MgO), sulphur trioxide (SO_3), sodium oxide (Na_2O), potassium Oxide (K_2O) and phosphorus oxide (P_2O_5). Also loss on ignition (LOI), free lime and insoluble residue (IR) were also determined.

Results and Discussion

Chemical composition of softwood ashes and clinker

Table 2 shows the mean value of elemental oxides present in the AOA, sample by using X-ray fluorescence analyser (Model: QX 1279) as specified in BS EN 196-2: 1995. The results indicate that the samples of ash from AOA had total percentage of silica (SiO_2), Alumina (Al_2O_3) and Ferric oxides of 70.50. This value was higher than the value (61.18) reported by Raheem and Adenuga (2013) in which the type of wood that produces the ash was not known. This indicates that the ash is a good pozzolanic material in accordance with ASTM C 618, 2001 a requirements which a good pozzolan for manufacture of blended cements should meet.

Table 2: Percentage composition of softwood ash

Chemical constituents	Percentage Compositions (%)			
	AOA 1	AOA 2	AOA 3	Average
SiO_2	62.05	62.10	62.00	62.05
Al_2O_3	5.55	5.57	5.56	5.55
Fe_2O_3	2.90	2.89	2.88	2.89
CaO	10.00	10.00	10.00	10.00
MgO	3.60	3.59	3.61	3.60
SO_3	1.45	1.44	1.46	1.45
K_2O	5.79	5.76	5.76	5.77
Na_2O	0.35	0.36	0.54	0.35
Total $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$	70.40	70.56	70.44	70.50

Table 3 shows the chemical composition of the clinker used. The values obtained for the elemental oxide are in agreement with range of values reported by Adesanya and Raheem (2009). The composition also satisfied the requirement in ASTM C 150: 1994 and NIS 439:2000. Thus the clinker is quite suitable for cement production.

Table 3 Chemical composition of clinker used

Chemical Composition	Percentage Composition(%)			
	Sample 1	Sample 2	Sample 3	Average
SiO ₂	20.22	20.25	20.45	20.30
Al ₂ O ₃	5.30	5.45	5.65	5.47
Fe ₂ O ₃	3.43	3.26	3.72	3.47
CaO	66.00	64.85	66.85	65.90
MgO	2.28	1.98	1.80	2.02
SO ₃	2.14	2.14	2.23	2.17
Na ₂ O	0.15	0.15	0.15	0.15
K ₂ O	0.29	0.32	0.23	0.28
P ₂ O ₅	0.17	0.13	0.21	0.17
LOI	1.33	1.30	1.30	1.31
LSF	95.93	95.73	96.04	95.90
AR	1.55	1.64	1.45	1.55
SR	2.23	2.35	2.17	2.25
Free lime	1.11	1.05	0.94	1.03

Chemical composition of AOA blended cements

The chemical composition of AOA blended cements produced by using the ash and clinker presented in Table 2 and 3 above are presented in Table 4. The silica content of the blended cements increased from 20.08% for 5% replacement to 21.15% for 50% replacement. This is in line with the findings of Adesanya and Raheem (2009) that reported increase in Silica contents of corn cob ash (CCA) blended cement as the percentage of CCA increases and also in line with Raheem and Kareem (2017) that reported increase in Silica contents of rice husk ash (RHA) blended cement as the percentage of RHA increases. AOA blended cements satisfied the minimum of 20% silica content requirements for Type II and Type IIA Portland Cement as specified by ASTM C 150: 1994.

Table 4 Chemical composition of AOA-blended cement

Oxide	Percentage composition (%)										
	0%	5%	10%	15%	20%	25%	30%	35%	40%	45%	50%
SiO ₂	20.15	20.08	20.16	20.18	20.22	20.24	20.40	20.62	20.80	20.90	21.15
Al ₂ O ₃	4.96	4.92	4.90	4.86	4.84	2.80	4.78	4.72	4.66	4.64	4.50
Fe ₂ O ₃	2.89	2.88	2.86	2.82	2.78	2.76	2.72	2.68	2.64	2.60	2.58
CaO	63.66	63.62	63.52	63.44	63.20	63.00	62.68	62.44	61.98	61.50	61.00
MgO	1.78	1.80	1.84	1.88	1.92	1.96	2.00	2.20	2.30	2.40	2.48
SO ₃	2.26	2.28	2.32	2.36	2.38	2.42	2.46	2.48	2.52	2.56	2.58
K ₂ O	0.21	0.22	0.24	0.26	0.30	0.34	0.38	0.42	0.50	0.60	0.90
Na ₂ O	0.03	0.02	0.02	0.02	0.01	0.01	0.01	0.00	0.00	0.00	0.00
Na ₂ O	0.00	0.01	0.01	0.01	0.02	0.02	0.03	0.03	0.09	0.10	1.14
Free Lime	2.10	1.91	1.89	1.82	1.72	1.70	1.67	1.65	1.58	1.54	1.46
LSF	0.99	0.99	0.99	0.99	0.98	0.98	0.97	0.96	0.95	0.93	0.92
SR	2.56	2.57	2.59	2.62	2.65	2.68	2.72	2.78	2.85	2.88	2.88
AR	1.71	1.70	1.71	1.72	1.74	1.74	1.76	1.76	1.77	1.78	1.74
C ₃ S	67.66	67.60	67.40	67.20	66.88	66.40	66.10	65.80	65.30	64.00	62.00
C ₃ A	8.26	8.20	8.16	8.00	7.88	7.86	7.82	7.80	7.76	7.70	7.20
C ₄ AF	8.80	8.84	8.82	8.78	8.74	8.60	8.65	8.60	8.56	8.52	8.00

As the percentage of AOA increased, there was a decrease in the contents of alumina and ferric oxide of AOA blended cements. Alumina contents decreased from 4.92 to 4.50 and ferric oxide decreased from 2.88 to 2.58 for 5% to 50% replacement, respectively. However, all the blended cements satisfied the maximum of 6.00% alumina content requirements for Type II and Type IIA Portland cement specified by ASTM C 150-02.

Calcium oxide (CaO) and lime saturated factor (LSF) follow similar trend with alumina and ferric oxides. CaO contents of AOA blended cements decreased from 63.62 to 61.00 as the percentage of AOA was increased from 5%

to 50% replacement. The LSF decreased from 0.99 to 0.92 for 5% to 50% replacement, this means that addition of AOA reduces the lime content of the AOA blended cements. This is in line with the findings of Adesanya and Raheem (2009) and Raheem and Kareem (2017). CaO and SiO₂ are responsible for the formation of tricalcium silicate (C₃S or 3CaO.SiO₂) and Dicalcium silicate (C₂S or 2CaO.SiO₂) in cement and all other clinker minerals. These two compounds are responsible for the strength in the late or early part of the concrete (Taylor, 2004).

The minor oxide compounds of Na₂O and K₂O known as alkalis for AOA blended cements ranged from 0.02% - 0.00% and 0.22% - 0.90 %, for 5% to 50% replacement, respectively . These values are higher than those of the control which are 0.03% for Na₂O and 0.21% K₂O. These amount of alkalis are lower compared to Adesanya and Raheem (2009) and Raheem and Kareem (2017). Higher alkalis in cement are undesirable as it causes damage to kiln and attack reinforced concrete as reported by Taylor (2004). It also results in alkali –silicates reaction (Dabai *et al.*, 2009). The loss on ignition (LOI) of the AOA-blended cements was higher than that of the control and ranges from 1.45% to 2.90% as against the 1.28% for the control. According to Adesanya and Raheem (2009) the higher the LOI, the higher the organic content of the cement which will result to lower binding power of the cement. However, all the value of LOI of AOA blended cements are lower than the recommended limit of 5% by NIS 439:2000 requirements. This means that AOA blended cement have lower organic content and good binding power.

Physical properties of AOA blended cements

Table 5 shows the results of fineness and residue on 45µm sieve of AOA blended cements. The fineness of AOA blended cements ranges from 353 m²/kg for 5% to 535 m²/kg for

50%. As the percentage of AOA is increased, the fineness of AOA blended cement also increases because AOA is of lower density compared to OPC-clinker and gypsum. AOA blended cements produced satisfied the 250 m²/kg and 280 m²/kg minimum fineness specified by NIS 439:2000 and ASTM C 150:2000, respectively. The AOA blended cements residue on 45µm sieve increases from 19.10% to 29.00% for 5% to 50%, replacement as AOA is increased. The coarseness was attributed to the clinker component which was harder to grind compared with the pozzolan. Hence, it could be concluded that the relative hardness of the pozzolan significantly influences the increase in the setting time of the produced cements.

Table 5: Physical characteristics of AOA blended cements

Percentage replacement of AOA (%)	Fineness (m ² /kg)	Residue on 45µm sieve (%)
0	352	13.40
5	353	19.10
10	355	19.70
15	379	20.00
20	410	20.50
25	420	21.50
30	469	22.75
35	500	23.75
40	515	25.55
45	520	27.00
50	535	29.00

The initial and final setting time for AOA blended cements is shown in Figure 1. The initial and final setting time increased from 50 min to 135 min and 75 min to 265 min, respectively as the percentage of AOA replacement increases from 5% to 50%. AOA blended cements satisfy the NIS 439:2000 requirement of 45 min minimum initial setting time and maximum of 10 hrs final setting time. The variation increase in setting time as percentage replacement of AOA increased lead to slowing down of hydration process. The slow hydration is an indication of low rate of heat development, which is one of the notable characteristics for which pozzolan cement are known and is of great importance in mass concrete construction where low rate of heat development is very essential as it reduces thermal stresses.

Fig 1. Effects of initial and final setting time on AOA blended cements

Figure 2 show the variation of heat of hydration of AOA blended cement with different percentage replacement ash for duration of six hours. It was revealed that the temperature of the control sample increases consistently while all AOA replacements levels were constant for some hours before showing slight changes in temperature. This means that, the control sample generated more heat of hydration at early stage while AOA blended cements produced low heat of hydration at early stage. It can also be seen that as the percentage replacement of AOA increases, the heat of hydration of all the wood ash blended cements reduces.

Fig. 2: Heat of hydration of AOA blended cements

Conclusion

The following conclusion re draw from the study:

- AOA is a suitable material for use as a pozzolan, since it satisfied the requirement for such a material by having the sum of SiO_2 , Al_2O_3 and Fe_2O_3 of more than 70%.
- The addition of AOA as pozzolan in blended cement increases marginally the oxide composition of SiO_2 and decrease slightly that of Al_2O_3 , Fe_2O_3 and CaO .
- AOA blended cement satisfied BS 12:1991, ASTM C 150:1994 and NIS 439:2000 requirement for up 20% replacement of ash.
- As AOA blended cement have higher setting time than the control hence, they are most applicable where low rate of heat development is required. This shows that all the blended cement are good as low heat cement.

AOA blended cements is recommended for use where low heat cement is applicable such as dam construction.

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