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Co-fired Ghanaian clay-palm kernel shells pozzolan: Thermogravimetric, ^{29}Si and ^{27}Al MA NMR characteristics

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HIGHLIGHTS

- The formulation of pozzolan from co-fired clay and palm kernel shells is very uncommon.
- Co-fired clay and palm kernel shells proved to have superior pozzolanic properties than only calcined clay.
- Quantitative measurements based on ^{27}Al and ^{29}Si MAS NMR provided detailed information on the nature of hydration products which was used to explain strength performance of the pozzolan.

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ABSTRACT

Pozzolanic materials are well known to improve the mechanical and durability properties of cement based products including concrete, mortar and paste. This has therefore made pozzolans widely accepted for construction. In this work pozzolans were produced from a mixture of clay and palm kernel shells. Thermal gravimetric analyzer (TGA) was used to determine the lime consumption pattern of the calcined clay pozzolan whereas the ^{29}Si and ^{27}Al solid state magic angle spinning nuclear magnetic resonance (MAS NMR) was used to determine the aluminate and the silicate phases of the hydrated product. The TGA results showed that the calcined pozzolan containing palm kernel shells had a higher lime consuming pattern than the calcined clay and Portland cement. The ^{27}Al MAS NMR showed that the calcined clay/palm kernel shell pozzolan produced stable monosulphate compounds at the octahedral environment. The ^{29}Si MAS NMR results also proved that additional calcium silicate hydrates were formed in the cement containing pozzolan than the Portland cement. The formation of stable monosulphates coupled with formation of additional silicate hydrates are the reasons for strength enhancement of the calcined materials than Portland cement.

1. Introduction

The utilization of pozzolanic materials in the construction industry has attracted considerable interest among construction professionals and researchers worldwide. This is because pozzolanic materials are well known to improve the mechanical and durability properties of cement based products including concrete, mortar and paste [18,29,19,11,28]. Moreover, the utilization of pozzolans are well documented to minimize energy consumption in cement producing plants as well as their carbon dioxide emissions, a major contributor to global warming [13,14,24]. Cement production generates between 5 and 8% of the total carbon emissions worldwide [6,15,34]. A pozzolanic material is defined as a siliceous or siliceous and aluminous material, without direct cementitious value, but will, in the presence of moisture, reacts chemically with calcium hydroxide (at ordinary temperatures) to form compounds possessing cementitious properties [21,31].

The use of fired clays pre-dates the world's industrial revolution [26]. Fired clays were ground and mixed with lime to produce structural materials in ancient times [5,32]. The early Roman empire was producing strong cementing material used for construction from the combination of lime and a pozzolan sourced from a volcanic ash deposit in a town called Pozzuoli in Italy [21]. Post industrial revolution has also seen major advancements regarding the use of fired or calcined clays as cement partial replacement materials from different regions of the world

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[12,32]. Many of the research works on calcined clays are focused more on high grade kaolinitic clays [8,23]. Clays with a kaolinitic content greater than 65% are known/defined as high grade kaolinitic clays [2]. Heat treated high-grade kaolinitic clays from 600 to 850 °C also known as metakaolins possess high pozzolanic reactivity with Portland cement as compared to other clay resources on the earth crust which include montmorillonite and illitic clay types [12]. However, the availability of high graded kaolinitic clays are of limited quantity on the earth crust. This therefore has provided the avenue for researchers to investigate the suitability of low grade kaolinitic clays such as montmorillonite and illite clays as good pozzolanic materials. Literature has documented many successful works from other clay resources aside high grade kaolinitic clays [1,7].

Literature on co-fired clay and palm PKS is very uncommon. However, Bediako et al. [7] have shown that the addition of 20 wt% of PKS in low grade kaolin clay yielded the optimum strength activity index. The investigations also confirmed that the optimum Portland cement replacement was 20 wt% of the calcined material. Fig. 1 below presents the results of the compressive strength of the calcined materials. The behavior of the blended cement mortar mixture compared with Portland cement mortar was attributed to the pozzolanic activity of the calcined product. Pozzolanic activity enhances compressive strength and durability of concrete through lime consumption and pore size refinement. Lime generated from cement hydration when consumed by a reactive pozzolan leads to the formation of secondary aluminate and silicate hydrates. The formation of these hydrates creates cement matrix densification. The product formed fills capillary pores which are usually created due to cement hydration. The pore size refinement mechanism reduces the permeability of the cement system [31].

The assessment of the pozzolanic activity of pozzolanic materials are performed in two ways: the indirect and the direct method [31]. The indirect method assesses physical changes due to pozzolanic reaction. This is usually determined using the technique of compressive strength, electrical conductivity and conduction calorimetry. The direct method also monitors the generation and consumption of lime by pozzolanic reaction and this method is analyzed using the X-ray diffraction and thermogravimetric analysis technique.

The earlier studies shown by Bediako et al. [7] used strength test (strength activity index and compressive strength), an indirect method to analyze the pozzolanic activity of the co-fired pozzolanic material. In the earlier studies, the major gaps in the work were: (1) the effect of PKS in the fired clay on hydration of cement and (2) the nature of hydration products formed from the reaction between Portland cement and the calcined material. This work seeks to fill these gaps. The main objective of the study is to investigate the pozzolanic activity of co-fired clay and palm kernel shell mixtures. To achieve the main objective, lime generation and consumption through hydration and pozzolanic reaction were performed with the TGA. The nature of hydration products was also assessed with the ^{29}Si and ^{27}Al solid state magic angle spinning nuclear magnetic resonance (MAS NMR).

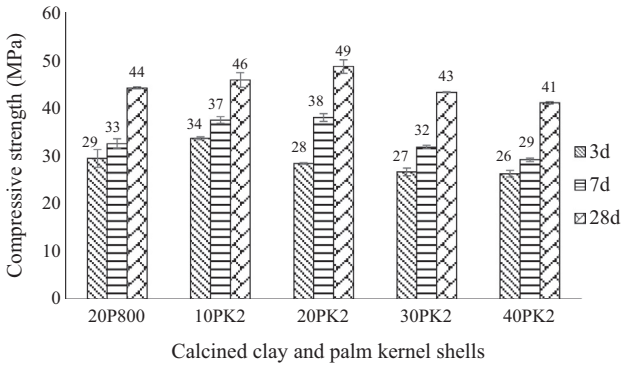

Fig. 1. Compressive strength of calcined clay and palm kernel shells.

2. Material and methods

2.1. Materials

The materials used for the study ASTM C150 Portland cement meeting both Type I and Type II classifications, clay, palm kernel shells, high range water reducer and potable water. The Portland cement was Ash Grove type obtained from Chanute, Kansas, United States. The clay was obtained from Nyamebekyere in the Ashanti region of Ghana. The area for the clay source has abundant of clay deposits which have been left untapped. The palm kernel shells were sourced from Konongo in the Ashanti region of Ghana. Natural graded silica sand which conformed to ASTM C778 was used whereas potable water from the running tap of University of Missouri-Kansas City (UMKC) in United States was used. Table 1 shows the physical and chemical composition of the Portland cement and the calcined clay (See Table 2).

2.2. Methods

2.2.1. Production of co-fired clay and palm kernel shells

The clay was air-dried for about 3 days and then milled into powder using a hammer mill. Palm kernel shells were also milled with the hammer mill into smaller particles. Clay and PKS were proportioned based on weight. PKS were used to replace 20 wt% of the powdered clay, mixed together to form clay-PKS mixtures. Approximately 5 kg of a total mass of clay-PKS mixture was formed. The mixture was used to produce small round ball i.e. nodules using an electric nodulizer and was labelled as 20PK2. The nodules produced were air-dried for about 24 h. The dried nodules were placed in a ceramic bowl and transferred into a laboratory electric furnace (Barnstead Thermolyne 6000) which was operated at 800 °C. The bowl and its content remained in the furnace for three hours at that temperature. After the 3 h the furnace was switched off and the bowl and its content left to cool in the furnace for about 24 h. The cooled pellet was then removed from the bowl and milled into fine powder particles using a laboratory hammer mill. The powder material was then sieved through the 75 μm sieve size. The powder samples that passed through the sieve were selected and used for the work.

2.2.2. Sample preparation for TGA and Al/Si MAS NMR studies

Samples used for TGA and Al/Si MAS NMR studies were obtained from the binder paste. The binder paste was prepared based on the optimum compressive strength value obtained in Bediako et al. [7]. As already indicated, the 20% of the calcined material used to replace Portland cement by weight produced the optimum mortar mixture. The binder paste was also prepared by replacing Portland cement with 20% by weight of the co-fired material. A paste of normal consistency was obtained from the mixture between Portland cement and the co-fired powder material. The consistency of the binder paste was performed in accordance with ASTM C187. For the Portland cement, the normal consistency was obtained by the addition of potable water to the cement. However, with cement and pozzolan mixtures, the consistency was obtained by the addition of water and iterative addition of HRWR. Paste of normal consistency was cured under damp burlap for 24 h. After this, the hardened paste was removed from the Vicat mould. The hardened

Table 1
Properties of Portland cement and calcined clay.

Property	PC	Calcined Clay
Physical		
Fineness (m^2/kg)	401.7	420
Specific gravity	3.13	2.61
Chemical		
SiO_2 (%)	20.49	61.89
Al_2O_3 (%)	4.26	13.51
Fe_2O_3 (%)	3.14	5.84
CaO (%)	63.48	0.21
MgO (%)	2.11	1.74
SO_3 (%)	2.9	0.14
$Na_2O + K_2O$ (%)	0.49	1.21
LOI (%)	2.2	10
Mineralogy		
C_3S (%)	56	
C_2S (%)	15	
C_3A (%)	6	
C_4AF (%)	9	

Table 2
Decomposition of samples occurring at temperatures T_b and T_c.

Mix	Decomposition (mg)					
	T_b			T_c		
	3d	7d	28d	3d	7d	28d
Control	3.346834	3.90209	4.183578	2.238329	3.05073	2.778645
20P800	4.060709	4.541207	3.182669	5.893873	4.822303	2.621022
20PK2	3.207856	3.097345	3.470214	3.829787	2.286136	1.908618

paste was sawn into three portions and cured in lime saturated water for 3, 7 and 28 days. After each curing period, the specimen was dried in an electric oven at 80 °C for about six hours. The dried specimen was removed from the oven and then ground into fine particles, and then sieved on the 75 μm sieve size. About 15 g of the undersize sieved sample were collected and placed in a centrifuge bottle. The hydration of the sieved sample was stopped by adding methanol into the bottle and its content. The centrifuge bottle and its content were then placed in the oven at 80 °C for drying. The dry samples were used for TGA and Al/Si MAS NMR studies.

2.2.3. TGA test on hydrated samples

Approximately 35 mg of the hydrated samples were used in a Mettler Toledo TGA/ SDTA 851 e analyzer heated to 750 °C, ramping at 10 °C per minute in N_2 gas. The content of calcium hydroxide generation as a results of Portland cement hydration and calcium hydroxide fixation also as a results of the degree of pozzolanic reaction were calculated following Yu et al. [36] and Poon et al. [27]. These formulae are given in Eqs. (1) and (2).

$$Content\ of\ CH = \left(\frac{T_b}{18} + \frac{2}{3} \times \frac{T_c}{44}\right) \times 74 \quad (1)$$

$$\%\ Fixation\ of\ Ca(OH)_2 = \frac{Ca(OH)_{2i} - Ca(OH)_{2t}}{Ca(OH)_{2i}} \times 100\% \quad (2)$$

T_b isthe decomposition occurring at 400–550 °C, and T_c is the decomposition above 550 °C. From experimental studies Yong-Xin [35] stated that two-thirds in T_c that decompose is from carbide and it occurs at temperatures between 400 °C and 550 °C. For lime fixation or consumption, $Ca(OH)_{2i}$ the initial amount of calcium hydroxide in the sample, and $Ca(OH)_{2t}$ the amount of calcium hydroxide consumed by cement/pozzolan at a determined curing time (t).

2.2.4. Al/Si MAS NMR test

Tecmag Apollo Console (Houston, TX) with 8.45T magnet and homebuilt, single channel, 4 mm wide-bore NMR probe was used to determine ^{27}Al and ^{29}Si spectra. About 90 mg of sample was taken for each analysis and signal represented as chemical shift value; δ: ppm. The ^{27}Al and ^{29}Si Larmor frequencies were 93.074 MHz and 70.958 MHz respectively. ^{27}Al spectra were acquired with MAS spinning frequency, last delay and 90° pulse length of 8 KHz, 1 s and 2.5 μs, respectively. ^{29}Si spectra were acquired with MAS spinning frequency, last delay and 60° pulse length of 8 kHz, 20 s and 5.5 μs, respectively. Aluminum nitrate [$Al(NO_3)$] and Tetramethyl silane (TMS) were used as reference compounds for ^{27}Al and ^{29}Si spectra respectively. All experiments were performed at ambient temperature without any corrections for sample heating.

3. Results and discussions

3.1. TGA studies

Table 1 presents the decomposition of the samples at temperatures T_b and T_c. The Table 1 was used to deduce the content of CH using Eq. (1). Fig. 2 shows the degree of pozzolanic reaction of Portland cement (Control) and the mixtures between Portland cement and two calcined products, calcined clay and calcined clay and palm kernel shell mixtures which were denoted as 20P800 and 20PK2. The figures show both negative and positive values on the y-axis. Negative values denote consumption of calcium hydroxide (CH) below the control paste whereas the positive values denote consumptions of CH above the control paste. The CH consumption of 20PK2 peaked at 7 days and remained almost constant to the maximum age of 28 days whereas the calcined clay peaked at the maximum 28 days. This indicated that pozzolanic reaction occurs earlier and is rapid with the inclusion of palm kernel shells into clay than calcined clay (20P800) and the control. This trend is like the use of silica fumes at early ages and is attributed to their excellent pozzolanic reactivity [33].

The rapidity of the pozzolanic activity of 20PK2 is attributed to early formation of secondary calcium silicate and aluminate hydrates more than 20P800 and the control. The formation of the secondary hydrates enhances compressive strength and minimize porosity of the cement system. The TGA results shows that at the early 3 and 7 days of hydration, 20PK2 attains higher strength values than the control and the calcined clay (20P800). The degree of pozzolanic reaction of 20P800 and 20PK2 at 28 days were very similar, however were all greater than the control. This shows that the late age strength and pore refinement characteristics could be very similar between 20P800 and 20PK2. Lam et al. [20] and Poon et al. (2001) have indicated from their studies that higher degree of pozzolanic reaction is attributed to pozzolanic reaction. The 28 days' results obtained from the TGA studies point out that both calcined products (20PK2 and 20P800) should have higher strength properties than the control. This is in line with Bediako et al. [7].

3.2. ^{27}Al and ^{29}Si MAS NMR studies

3.2.1. ^{27}Al MAS NMR

Fig. 3(A, B, C) presents the ^{27}Al solid state MAS NMR spectra analysis of hydrated cement (control) and 20PK2. Figures A, B and C under Fig. 3 represent hydrated samples at 3, 7 and 28 days. The aluminate phases produced in cement or cement/pozzolan system involves calcium aluminate hydrate (CAH), ettringite (Aft) formed from an initial hydration of C_3A and later converts into a

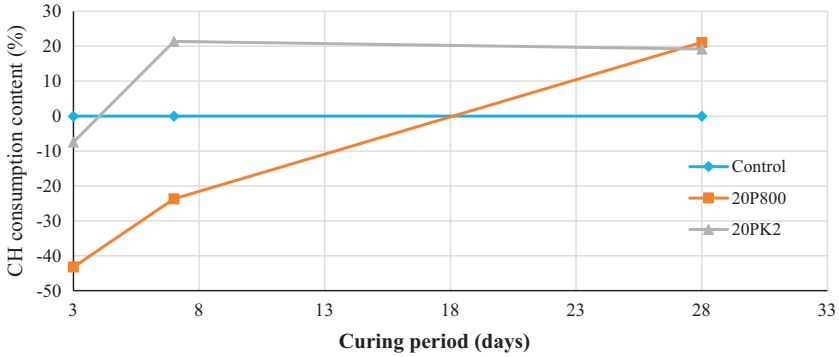

Fig. 2. CH consumption of control, calcined clay and calcined clay/palm kernel shells.

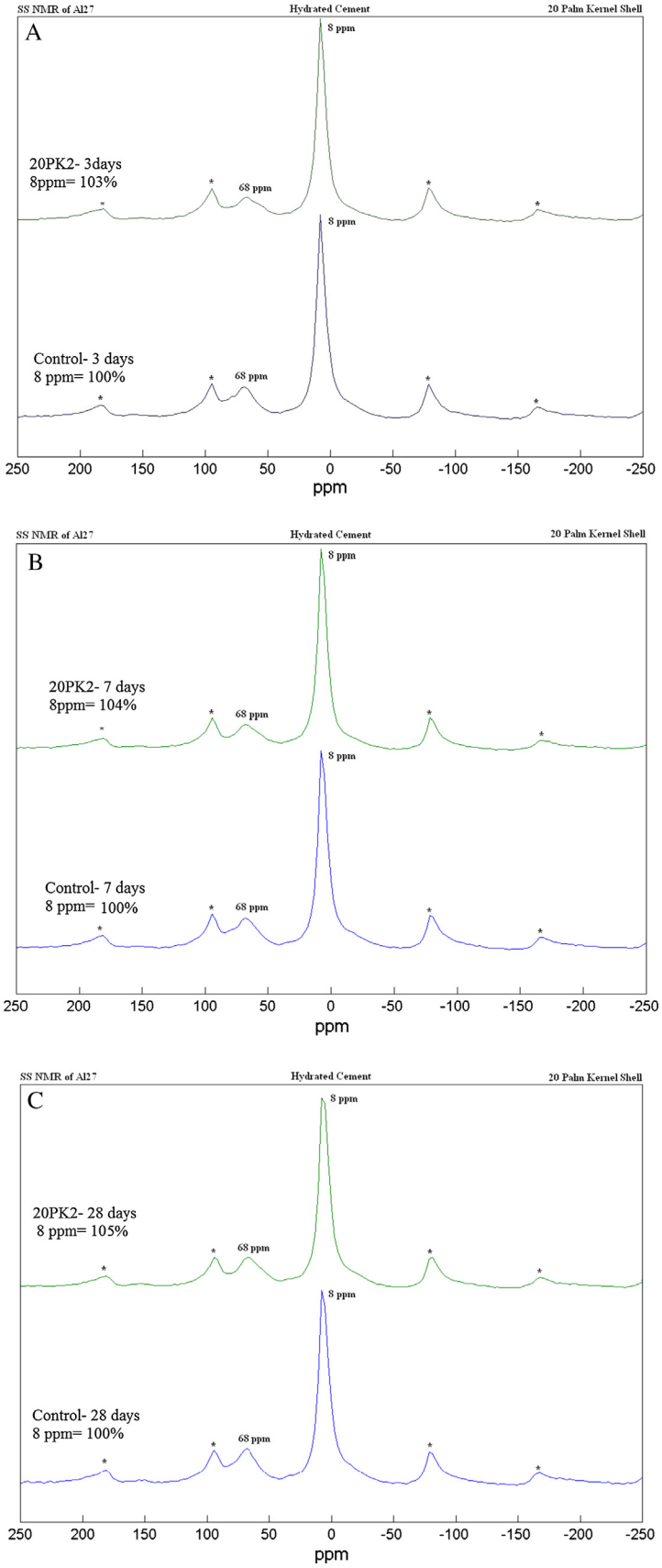

Fig. 3. ^{27}Al MAS NMR of the control and 20PK2, A-3 days, B-7 days and C- 28 days.

thermodynamically stable monosulphate (AFm). Generally, two distinct peaks are seen from the figure occurring at 68 ppm and 8 ppm. The chemical shift at 68 ppm represents the four coordinated aluminium environment ($Al^{[iv]}$) whereas the chemical shift at 8 ppm represents the six coordinated aluminium environment ($Al^{[vi]}$) [4,16]. Chemical shift around 68 ppm shows Al substitution in the calcium silicate hydrate (CSH) in the tetrahedral environment of Al, and produces a metastable form of hydro garnet or calcium aluminosilicate hydrate (CASH) [3,10]. The chemical shift around 8 ppm corresponds to thermodynamically stable monosulphates (AFm) occurring at the $Al^{(vi)}$ environment [4,30]. In a hydrated state, usually the aluminate phase shift from $Al^{(iv)}$ to $Al^{(vi)}$ [9].

Generally, as hydration progressed from 3 days to 28 days, the intensities of both the tetrahedral and octahedral Al environments increased progressively. This indicate that the inclusion of the calcined material (20PK2) provided more aluminium phase in the tetrahedral environment that dissolved in the alkaline environment to form a stratlingite (C_2AH_8), a stable monosulphate phase (AFm) containing Si substituted with Al [4,30]. The dissolution process shows the occurrence of pozzolanic reaction. Fig. 3A and B show that 20PK2 attaining 103% and 104% peak intensities respectively at the octahedral environment, a little bit high than the 100% intensity of the control paste. This indicate that 20PK2 had a rapid pozzolanic activity at the early ages of 3 and 7 days which confirms the results of the TGA.

The AFm phase in the tetrahedral Al environment, a metastable state shown in the figure transformed into a well crystalline cubic AFm phase as monosulphates in the octahedral ^{27}Al environment indicated at the chemical shift of 8 ppm [4,30]. The well crystalline cubic AFm phases also increased in intensities with hydration periods at the ^{27}Al octahedral environment. It was 103% at 3 days, then to 104% and 7 days and 105% at 28 days. This shows there were a little bit more of Al^{3+} substitution for Si^{4+} with time, dissolving in the alkaline environment to form calcium aluminosilicate hydrates. Chenguang et al. [10] mentioned that Al^{3+} substitution for Si^{4+} promotes the stability of calcium silicate hydrates. The increase in stable compounds in the aluminate phases in the CSH structure explain the reason for the high strength of 20PK2 more than the control (CON).

3.2.2. ^{29}Si MAS NMR studies

Fig. 4(A, B, C) presents ^{29}Si MAS NMR spectra analysis of the control and 20PK2 hydrates. The figure denoted as A, B and C represents paste samples hydrated at 3, 7 and 28 days respectively. The ^{29}Si MAS NMR provides information on the degree of polarization of the silicate phases. The theory of pozzolanic reaction has shown that there is always the formation of secondary calcium silicate formation that enhances strength and durability of mortars and concretes. The extent of polarization is usually denoted as Q^n, where Q is the central silicon unit (SiO_4) and n is the number of silicon units (SiO_4) connected to the central silicon unit [25]. Increase in polarization of the silicate phases usually increases the n units [22]. This gives a more negative chemical shift (electron rich field) due to polarization.

In Fig. 4A, the control sample resonated at −90 ppm, −99 ppm and −103 ppm. The chemical shifts that occurred at −90 ppm and −99 ppm represent Q^3 environment whereas the −103 ppm represents a Q^4 environment [17]. On the 20PK2 spectrum, an additional resonating point was observed at −97 ppm which represent a Q^3 as shown by Maclaren and White [22]. Moreover, there was a sharp peak at −99 ppm on the 20PK2 spectrum. This shows that the 20PK2 responded rapidly to pozzolanic reaction by form-

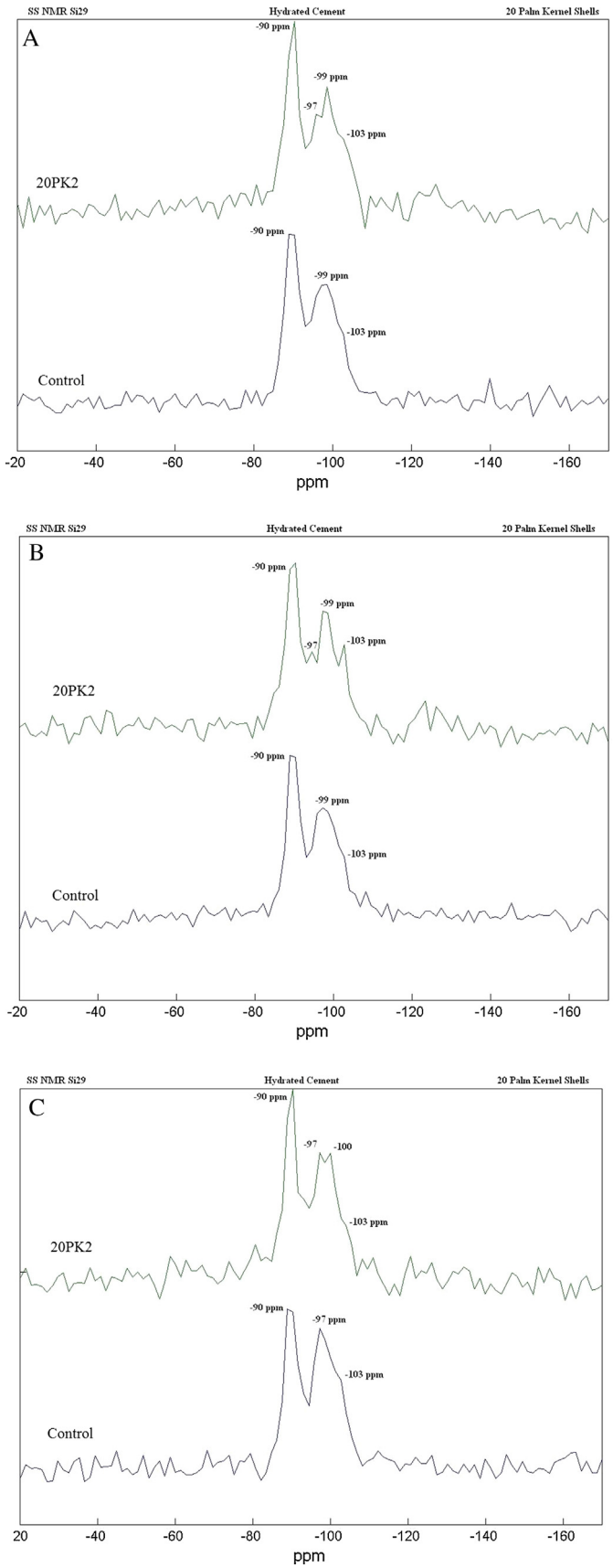

Fig. 4. ^{29}Si MAS NMR of control and 20PK2 hydrated paste; A- 3 days, B- 7 days. C- 28 days.

ing additional polarized phases. As hydration progressed to the period of 7 days (Fig. 4B), the chemical shifts shown on both spectra developed smaller sharp peaks, an indication of a progress in pozzolanic reaction which leads to the formation of condensed silicate phases. The sharp peak seen at −103 ppm on the spectrum of 20PK2 in Fig. 4B indicates an increase intensity, a sharp contrast shown on the spectrum of 20PK2 at 3 days shown in Fig. 4A. This confirms the formation of more silicate phases in the Q^4 environment as indicated by Maclaren and White [22], an indication of increased polarization and a progress in pozzolanic reaction. At 28 days of hydration, the chemical shift at −90 ppm on the control spectrum was maintained but with a formation of a small sharp peak. There was also a decrease in the chemical shift from −99 ppm on the 7 days' control spectrum to −97 ppm on the 28 days' control spectrum. This indicate a decrease in crystallinity. The chemical shift at −103 ppm on the control spectrum in Fig. 4C was a little intense than the one shown on the control spectrum in Fig. 4B. The decrease in crystallinity and the formation of more polarized phases indicate progress of cement hydration from a Q^3 to a Q^4 environment. On the 20PK2 spectrum in Fig.4C, additional chemical shift was noted at −100 ppm, a Q^4 environment. This shows that the addition of the calcined material to cement led to the formation of more polarized phases than the control. This explains the reason behind the high strength of the 20PK2 than the control at the late age of 28 days which is reported in Bediako et al. [7].

4. Conclusions and recommendations

4.1. Conclusions

The pozzolanic activity of calcined clay and palm kernel shell mixtures (20PK2) have been analyzed using thermal gravimetric analysis, ^{27}Al and ^{29}Si MAS NMR. The addition of the palm kernel shells – kaolin clay mixtures to produce a calcined pozzolanic product gives rise to more pozzolanic active phases than the solely calcined clay pozzolan. For this reason, a higher degree of pozzolanic reaction at 3 and 7 days for the calcined clay-palm kernel shell hydrated sample was observed in comparison with that of the calcined clay pozzolan hydrated sample: an observation that was confirmed via thermal gravimetry.

The inclusion of the calcined pozzolans in cement produced more aluminate phases in the tertrahedral environment which passed into solution to form more and stable monosulphates at the octahedral aluminum environment. This phenomenon increases the strength of the cement system.

In comparison with the control cement paste, the calcined clay-PKS pozzolan formed additional calcium silicate hydrates at every period of hydration (3, 7 and 28 days). This additional silicate hydrates formed in the cement-pozzolan mixtures further increases the strength properties of the cement system.

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