

INSIGHT INTO THE HYDRATION AND MICRO-STRUCTURAL PROPERTIES OF EXTRACTED STARCH FROM CASSAVA AND MAIZE ON CEMENT AND CONCRETE

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(Received 19 June 2018, Accepted 23 August 2018)

¹Abstract

This paper examines the mechanism of hydration and micro-structural characteristics of cement blended with starch obtained from cassava and maize. The dosages of cassava (CA) and maize (MS) starch added in different percentages (0, 0.5, 1.0, 1.5 and 2.0 %) by weight of cement to mixes of pastes and concretes. Automatic vicat needle apparatus was used to determine the setting times of cement pastes. Adiabatic calorimetry was utilized to quantify the total heat and rate of heat of evolution during hydration. Fourier transform infrared spectroscopy and morphology of the hydration products of the cement pastes provide clues on the cause of delays in hydration. The result showed that setting times, and dormant period of hydration was prolonged with shifts in peaks of hydration as concentration of starch increase within the first few hours.

Keywords: starch, cement, hydration, microscopy, FTIR spectroscopy, durability properties

1 INTRODUCTION

The idea of the production of green or sustainable concrete gives rise to more complex design mixes which include the use of various types of either mineral, chemical or organic admixtures in concrete. Some of these admixtures or additions to concrete may be by-products from other processes of production. A more fundamental understanding of the kinetics of hydration mechanism is required to present a more robust mix design and in the choice of the use of admixtures. Bullard et al. [1] pointed out that understanding of the hydration process at molecular level is helpful in providing information on the rates of reaction, diffusion, temperature and the influence of curing conditions of the concrete. Admixtures are meant to give some direct advantageous effects like air entrainment, workability, viscosity, acceleration, retardation, water reduction to the cementitious system according to Ramachandran et al. [2]. It can also influence the system indirectly by providing higher durability and strength among

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others. Water-soluble polymers are hydrophilic in nature by fixing water molecules in fresh concrete thus preventing evaporation and absorption into the surrounding porous material [3]. The ability to be able to control the rate of early reaction of freshly mixed concrete to maintain its fluidity and workability during the time of mixing, placement and compaction before setting of concrete cannot be overemphasized. Nonetheless, the complexity of the mechanisms of hydration procedure has not been fully comprehended. There is no specific concept to interpret observed stages of initial hydration process of cement according to Thomas [4]. For example, Perchard et al. [5] found yellow dextrin to retard the formation of portlandite for about eight hours after which the rate of formation turns out to be similar to that of pure cement. However, Perchard et al. [5] in the same investigation reported that starch ether to slow down the formation of portlandite for the entire test period of 24 hours of hydration though induction time was not affected.

Various authors such as Peschard et al. [5] reported that polysaccharides with a lower average molecular weight have stronger set-retarding ability; Uzoegbo [6] examined the hydration of blended cement in isothermal calorimetry for application in civil engineering works. Luke and Luke [7] brought to the fore the effect of sucrose on the retardation of concrete; Crépy [8] demonstrated the potential benefits of using organic admixtures in concrete; Akindahunsi et al., [9] showed the possibility of using starch modified concrete as a repair material. Akindahunsi et al. [10] work gave an insight into the influence of starch on some properties of concrete; Laberas-Zubiarte et al. [11] illustrated the effect of chitosan ethers on the fresh properties of cement mortars and Teixeira et al. [12] reported on the properties of thermoplastic starch from cassava among others. Zhang et al. [13] also carried a study on the influence of the use of saccharides (sucrose and aliphatic sugar alcohol) as set retarders on the process of hydration of cement and tricalcium silicate (C_3S). The authors found that the aliphatic sugar alcohol retard setting of both the cement, delay hydration during the dormant period by blocking the formation of calcium silicate hydrate nuclei during the stage two of hydration whereas hydration is accelerated in the course of stage three.

The products of hydration process of cementitious systems are the development and changes that occur at the microstructural level over time. The solid volume of cementitious system is increased as a result of the reaction of anhydrous cement with water during the hydration process. Scrivener [14] noted that the dense quantity formed is as a result of extra quantity that covers the spaces between cement grains. During hydration process in cement paste, the dominating reaction of C_3S yields C-S-H and CH. The microstructural phases of these hydration deposits are very clear: calcium hydroxide deposits are found mainly in pores filled with water while calcium silicate hydrate accumulations are seen around grains of cement. The essential characteristics of scanning electron microscope images of the important outline of microstructure of pastes and concrete can therefore be interpreted [14]. There is substantial information on rate and total heat of hydration at microstructural phase of development of fresh to hardened cementitious systems with admixtures. However, hydration and microstructural characteristics of extracted starch from cassava are scarce in literature hence; this study aims to fill some gaps. Starch can be extracted from cassava tubers or maize grains (by first peeling off the skin and washing in the case of cassava tubers), grinding, filtering which includes separation of starch from other contaminants in the solution. The wet starch material is then dried, milled and packaged. Starch has variety of industrial applications and in the construction industry it is used

as adhesive, gypsum binder, asbestos binder according to Satin [15] and modified starch is used in shotcrete applications to reduce rebound as reported by Mann et al. [16].

2 MATERIALS AND METHODS

2.1 Setting Time Tests

The tests for the determination of initial and final setting times for the different percentages of cassava and maize starches additions in cement were carried out under controlled humidity ($60 \pm 5\%$) and temperature ($23 \pm 2^\circ\text{C}$). The tests complied with the South African standard SANS 50196-3 [17] and EN 196-3 [18]. Standard mortar mixer set to EN mixing standard was used to carry out the mixing of the different cement pastes with various concentrations of starches. The setting times were determined using automatic vicat needle apparatus ToniSet Expert model 7320 manufactured by Toni Technik, Germany as shown in Figure 1. For each starch dosage, 500 g of cement and a measured quantity of water were mixed in order to achieve the required penetration range of between 4 - 8 mm, the mixing was done using ToniMIX mortar mixer. The dosages of starches (cassava (CA) and maize (MS)) added to the batches of mixes prepared were 0, 0.5, 1.0, 1.5 and 2.0 % by weight of cement respectively. The tests were conducted in a fully automated test set-up (Figure 1).

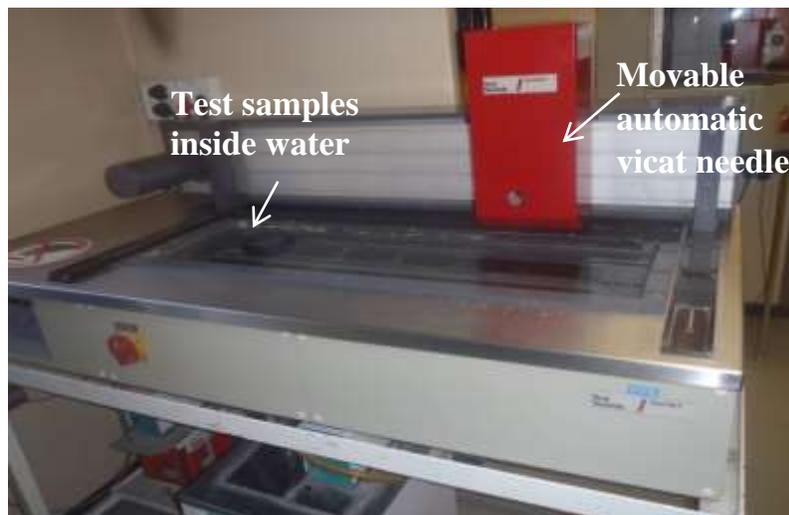


Figure 1: Automatic vicat needle apparatus ToniSet

2.2 Concrete mixes for heat of hydration

The typical composition of concrete mix for heat of hydration tests with different percentages of cassava and maize starch (0, 0.5, 1.0, 1.5 and 2.0%) addition is as shown in Table 1, the mix proportion will make a litre of concrete. Silica stones and sand were used in the mix because they are inert, making it possible to exclusively measure the heat evolved during hydration of cement. Three different sand sizes were combined in equal proportion. The mixing, compaction and setting up of the test in the water tank is usually less than five minutes in order to be able to capture some of the initial process of hydration of the cement. Prior to the start of any test, all the

constituents of the concrete mix are kept in the well-controlled temperature ($19 \pm 1^\circ\text{C}$) Calorimeter room for 24 hours for the materials to be able to attain same starting temperature with the Calorimeter. More information on the preparation of cassava and maize starch mixes can be found in Akindahunsi [19] and the schematic diagram of the adiabatic calorimeter used is shown in Figure 2 and further information about the set-up for use can be found in Ballim and Graham [20]. Figure 2 presents a schematic diagram of a test sample in the sample chamber placed in water tank. The sample is placed in an air chamber with a thermal probe inserted inside the concrete sample and the probe is connected to a controller for signal conditioning. The air chamber containing the sample is placed in the water tank and another probe placed by the side of the air chamber inside the water tank is connected to the controller. The temperature signal from the thermal probes is captured on the desktop computer via the controller that regulates the water temperature in the tank by switching the heater on and off in order to maintain the water temperature as that of the concrete sample.

Table1: Composition of typical concrete mix used in adiabatic tests

Materials	Quantity (kg/m ³)
Portland cement (CEM I 52.5N)	420
9.5 mm silica stone	1020
Fine silica sand (0.075mm to 0.3mm)	all in equal proportion
Medium silica sand (0.3mm to 0.65mm)	
Coarse silica sand (0.6mm to 1.5mm)	
Water	280

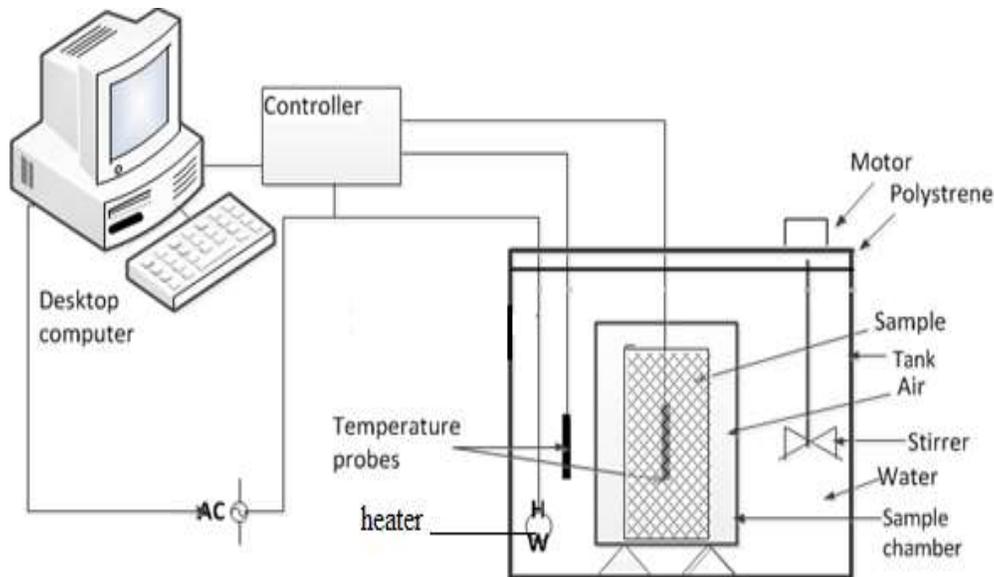


Figure 2: Schematic diagram of the adiabatic calorimeter used in the study

The test is set to run for about seven days or until no significant increase in temperature is recorded, whichever occurs first. The temperature variation in the sample is measured with time, $T(t)$. The total heat per unit mass of binder (q_t) released at any time (t) in the test is given by:

$$q_t = C_p \cdot (T_t - T_0) \cdot \frac{m_s}{m_c} \tag{1}$$

Where

q_t = total heat per unit mass of binder (kJ/kg)

C_p = specific heat capacity of the concrete (J/kg.K)

T_t = temperature of concrete at time t during the adiabatic test ($^{\circ}\text{C}$)

T_0 = sample temperature at the beginning of the test ($^{\circ}\text{C}$)

m_s = mass of concrete test sample (kg)

m_c = mass of the binder in the sample (kg)

The rate of heat of evolution is obtained by finding the first derivative of equation (1)

$$\dot{q}_t = \frac{dq_t}{dt} \tag{2}$$

The time component is converted to maturity time in order to accommodate the combined effect of temperature and time. Maturity, M , is given as:

$$M = \int_0^t f(T) \cdot dt \tag{3}$$

where

$f(T)$ = temperature function

Expressing adiabatic test ‘maturity heat rate’ (\dot{q}_M) as a function of cumulative maturity rather than time rate gives:

$$\dot{q}_t = \dot{q}_M \frac{dq_t}{dt} \tag{4}$$

The time-based heat rate as required in Equation (4) is then determined using Equation 6.5:

$$\dot{q}_t = \dot{q}_M \frac{dM}{dt} \tag{5}$$

Analysis of results from the adiabatic calorimeter test as the temperature was measured over n time periods, using the *Arrhenius* function is as presented by Naik [21] in equation (6):

$$t_{20} = \sum_{i=1}^{i=n} \exp \left[\left(\frac{E}{R} \right) \left(\frac{1}{293} - \frac{1}{273 + 0.5(T_i + T_{i-1})} \right) \right] (t_i - t_{i-1}) \tag{6}$$

where

t_{20} = equivalent maturity time (hours)

E = activation energy parameter (33.5 kJ/mol) (It has been shown that E varies with temperature during hydration, however, the variation is negligible that a single value is appropriate) (Bamford and Tipper, 1969)

R = universal gas constant (8.314 J/mol^oC)

T_i = temperature (°C) at the end of the i^{th} time interval, t_i

2.3 Scanning Electron Microscopy

To give an understanding of the formation and development of hydration products in order to have the microstructural information of the evolution of the products, 10 mm x 10 mm x10 mm cement paste cubes were cast. The addition of different starch concentrations used was same as that for the hydration mix proportions. Hu [22] and Garcia et al. [23] noted that scanning electron microscopy technique can be used to examine the influence of binder type, curing duration, effects of admixtures among others on the pore structure, hence its use in the study. The paste cubes were covered with polythene sheet after casting for 24 hours, demoulded and placed in a temperature-controlled curing chamber of 23 ± 2 °C. A set of two samples prepared for each starch concentration were cured for 1, 2, 3, 7 and 28 days. At the end of each curing age the samples were removed and placed inside a -70 °C freezer in order to stop the hydration process at the stated curing days. The samples were kept in the freezer for three days to ensure that any available water in the pore structures of the pastes were frozen. One advantage of this process is that the water in the pores of the cement pastes will only form amorphous ice which eliminate the possibility of any crack formations. At the end of three days of freezing, the required samples were weighed and kept in a freeze-drying facility to remove the amorphous ice in the samples. This method removes water vapours as the ice sublimates without going through the liquid phase. The samples were kept in this freeze-drying facility for five days and then weighed regularly until after a constant mass was obtained after the mass loss of the amorphous ice in the samples. The samples were thereafter kept in a silica gel container; this is to avoid absorption of moisture from the environment.

2.4 Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectroscopy is used as a vibrational method of identifying and validating material composition. Information on the characteristics of interaction between the starch and cement paste were explored using FT-IR spectroscopy. A Bruker Tensor 27 FT-IR spectrometer having instrument wavelength range lying between 400 and 4000 cm^{-1} was used to carry out tests on the pulverized cement pastes using same cassava and maize starch additions (0, 0.5, 1.0, 1.5 and 2.0%) by weight of cement used in the adiabatic calorimetry tests. The instrument was used to measure the fingerprint of samples with absorption peaks that correspond to the frequencies of vibrations between the bonds of the atoms making up the materials. In the use of FT-IR spectroscopy, infrared radiation was passed through the samples. Some of the infrared radiation were absorbed by the samples while some were transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the samples. The samples were scanned 67 times with a resolution of 1 cm^{-1} and the presented data are the average values.

3. RESULTS AND DISCUSSION

3.1 Results on Setting Times of Cement Pastes

The results of the setting times of starch admixed with cement pastes is as presented in Figure 3. The percentages of starch added to the cement mixes were (0, 0.5, 1.0, 1.5 and 2.0) and the first one without any starch addition represents the control. The setting times (initial or final) increase with increase in the percentage of starch addition in the cement irrespective of the type of starch used. Figure 3 showed that control has the lowest initial and final setting times followed by MS 0.5, MS 1.0, MS 1.5, MS 2.0, CA 0.5, CA 1.0, CA 1.5 and CA 2.0 respectively.

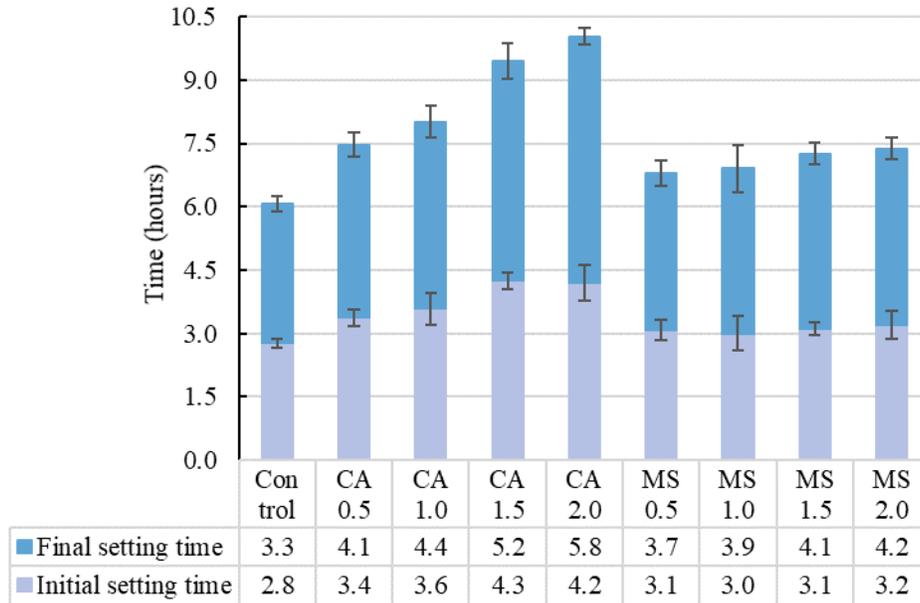


Figure 3: Setting time of cement with different concentrations of starch

Further observations from Figure 3 shows that increase in percentage of maize starch in cement leads to small progressive increase in both the initial and final setting times of the paste. However, increase in cassava starch percentage in the cement results much longer setting times (initial and final). When the same percentage of maize and cassava starch was compared, it is noticed that cassava starch pastes exhibited longer setting times. Cassava starch pastes exhibiting longer setting times may be due to the starch covering more of the surfaces of the cement grains. This is because it has larger surface area when compared to maize as illustrated in Akindahunsi [19].

The prolonged setting times of the cement pastes with starch additions may be attributed to starch covering the hydrating constituents and restricting the formation of products such as tricalcium silicate (C_3S) and tricalcium aluminate (C_3A) as noted by Ramachandran [24]. According to Brooks et. al. [25], it may also be due to adsorption of the admixture on the cement particle surfaces. It should however, be pointed out that even though some admixtures delay

setting times in cement mechanical properties such as strength and durability of the concrete are not negatively affected as can be seen in Akindahunsi and Uzoegbo [26].

3.2 Results of Periods and Peak Heat Rates

The peak heat rates are as presented in Figures 4 and 5. The peak heat rate observed in Figure 4 for the control is 3.7 W/kg and it occurred at 11.1 t_{20} hours. The peak heat for CA 0.5 is 3.5 W/kg at 13.1 t_{20} hours. The delay in maturity time (t_{20} hours) it takes to attain peak heat rate in comparison to the control is 2.0 t_{20} hours. The peak heat rate for CA 1.0 illustrated by Figure 4 is 3.6 W/kg at 13.2 t_{20} hours, when compared to the control, the peak heat rate is retarded by 2.0 t_{20} hours. Figure 4 shows the heat rate for CA 1.5 and from the Figure the peak heat rate recorded is 3.3 W/kg at 13.7 t_{20} hours with a prolonged peak heat rate of 2.6 t_{20} hours in comparison to the control. The peak heat rate for CA 2.0 is 3.2 W/kg at 14.6 t_{20} hours as seen in Figure 4 with a delayed peak heat rate of 3.5 t_{20} hours. It was noted that the peak heat rates for CA 0.5 and MS 0.5 were lower than CA 1.0 and MS 1.0 respectively (Figures 4 and 5). The subsequent CA 1.5 and MS 1.5 were higher than CA 2.0 and MS 2.0 respectively. The measured peak heat rate for MS 0.5 as indicated in Figure 5 is 3.5 W/kg at 12.7 t_{20} hours indicating a peak heat rate delay of 1.6 t_{20} hours when compared to the control. The peak heat rate for MS 1.0 as shown in the same Figure is 3.5 W/kg at 12.9 t_{20} hours with a delay period of 1.8 t_{20} hours. The peak heat rate for MS 1.5 occurred at 3.4 W/kg at 13.3 t_{20} hours. When compared to the control, a retarded peak heat rate time of 2.1 t_{20} hours is observed. The peak heat rate for MS 2.0 of 3.2 W/kg occurred at 14.8 t_{20} hours, with a lag peak heat rate time of 2.7 t_{20} hours.

3.3 Heat Rates and Induction Periods

The practical benefit of Portland cement concrete comes from the ability to be able to regulate the rate of early reaction of freshly mixed concrete in order to maintain fluidity for the length of time that it is going to be mixed, transported to the point of use, placed and compacted where it is required. Modifying the dynamics of this procedure to either prolong or reduce the setting time is one of the extremely significant roles of admixtures either inorganic or organic that are used in concrete on regular basis. The primary procedures that are critical to this process of reaction according to Thomas [4] and Bishop et al. [27] are not yet fully understood especially some organic materials that are not common in literature. Since no concept has fully explained all the major observations relating to the beginning of hydration process of cement due to its complicated nature and the interdependence of the chemical reactions, hence the need to know the peak heat rates for the concretes. The general observations from the results of the hydration test of starch concretes as seen in the results presented show that starch (cassava and maize) retards the time the concrete takes to attain the peak heat rate. This also confirms the result obtained from the setting time of cement pastes as presented in Section 3.1. Another major observation from the results showed that cassava starch has more retarding effect on the concrete than maize starch of the same quantity. Similar observation was also seen in section 3.1 with the effect of the starches on setting time of cement paste. The retarding effect of the starches on hydration of cement could be due to the shielding of CH surfaces which according to Cody et al. [28] delay the dissolution of the CH and the rate of cement setting reactions. Possibility of adsorption onto the hydrating phases was further supported by the obtained result of adsorption of potato starch onto lime particles by Izaguirre et al. [29] with the use of zeta potential. Schmidt [30] also confirmed the retarding effect of starch in his work. Young [31] pointed out that set-retarding admixtures have significant effect on the early hydration process of cement.

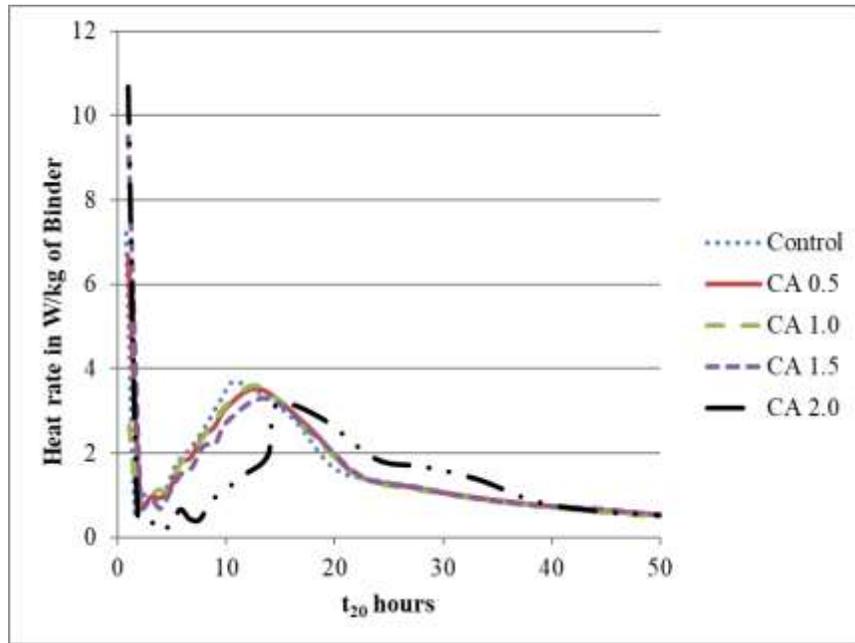


Figure 4: Heat rate measured for control and CA admixed with cement pastes

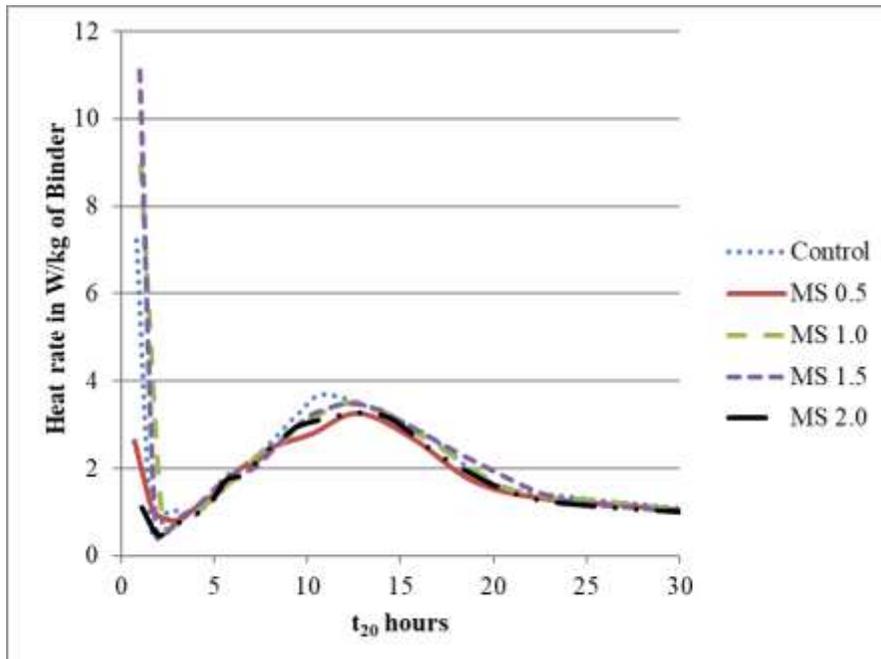


Figure 5: Heat rate measured for control and MS admixed with cement pastes

However, the author also revealed that at lower concentrations the effects of some retarders may not be noticeable in cement and in fact in some cases accelerate hydration of C_3A , this may justify why there is no significant difference in the effect of CA 0.5 and CA 1.0 on peak heat rate

and the maturity time. A similar situation is noticed in maturity time between MS 0.5 and MS 1.0. As the concentrations of starch increases, it prolongs the induction periods when compared to the control. Another similar admixture found to retard hydration of cement was sugar according to the findings of Juenger and Jennings [32].

It can also be seen in Figures 4 and 5 that with increase in concentrations of starches in concretes, the peak heat rates are progressively reduced during the hydration process with the exception of CA 1.0 and MS 1.0 which recorded higher peak heat rate of 3.58 and 3.50 W/kg respectively. The drop in peak heat rates with increase in concentrations of maize starch in concrete is also not as pronounced when compared to concretes with cassava starch of the same concentrations. Authors such as Peschard et al. [33] Cheung et al. [34] reported that retarding admixtures may affect different aspects of hydration processes. Some may affect induction period and accelerate the peak heat rates others may delay the peak heat rates as is the case with starches under investigation. In order to determine the statistical variability of the heat rates among the different concentrations of starch (cassava and maize) additions, one-way analysis of variance was performed on the results of the heat rates of hydration. The $F_{statistic}$ obtained was 0.86 and the calculated value of the $F_{critical}$ was 1.96, therefore, statistically there is no significant difference between the heat rates of the different concentrations of starch.

3.4 Total Heat of Hydration of the Concretes

The total heat evolved during the hydration tests conducted on the cements with different percentages of starch replacements are as illustrated in Figures 6 and 7. The results of the heat evolved by the different concretes show that none of the concretes evolved more than the estimated total heat by CEM I and high early strength Portland cement which are 375 and 390 kJ/kg respectively according to Owen [35]. It should be noted however, that the mechanical and durability properties of concretes admixed with starch not presented in this paper but can be found in Akindahunsi and Uzoegbo [26], shrinkage properties of concrete admixed starch can be found in Akindahunsi and Wolfram [36]. Also, statistical variability of the different mixes for total heat was calculated and the $F_{statistic}$ obtained was 0.17 while the $F_{critical}$ value calculated was 1.95, which implies that there is no significant difference between the total heat of the mixes.

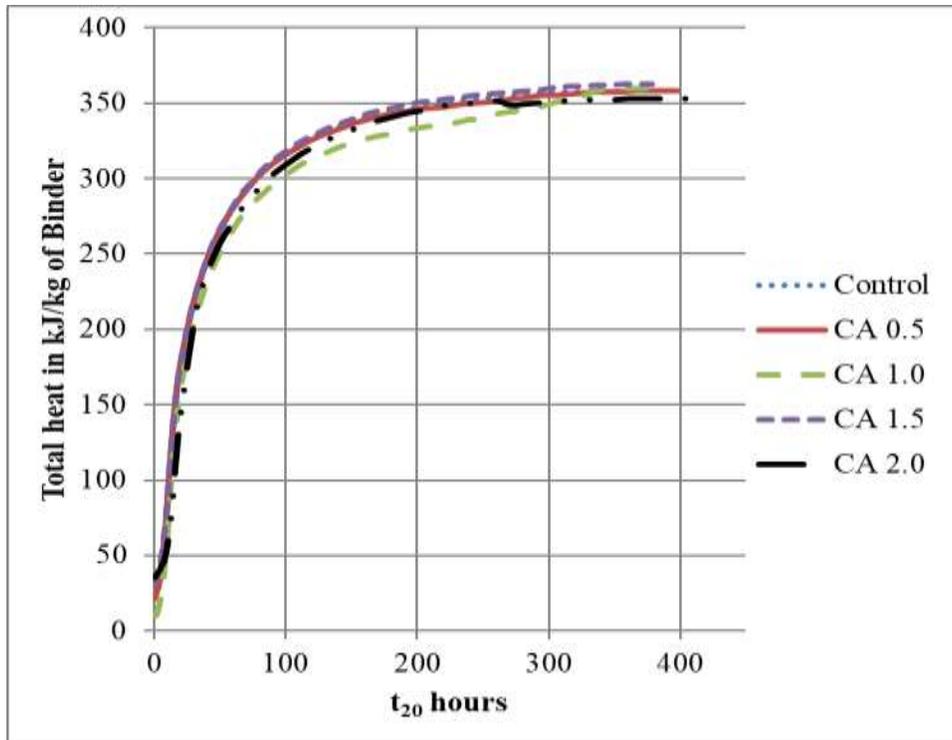


Figure 6: Total heat measured for control and CA admixed with cement pastes

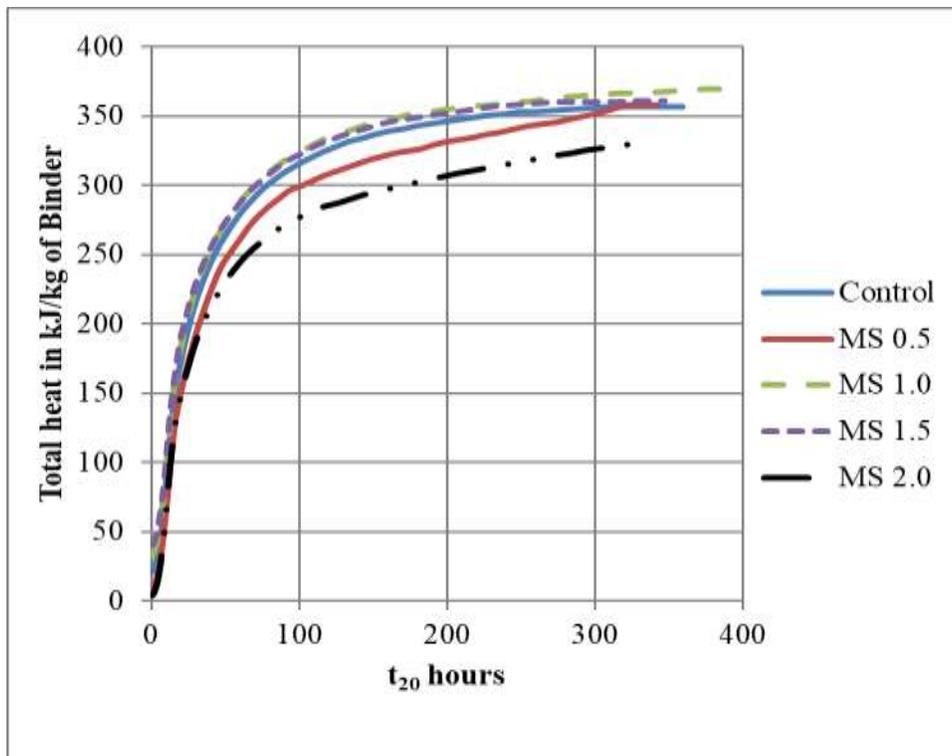
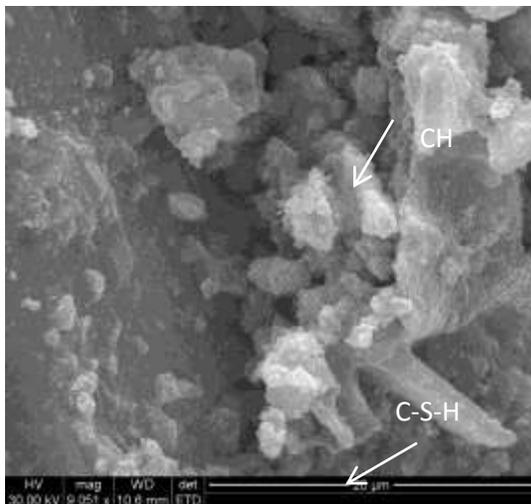


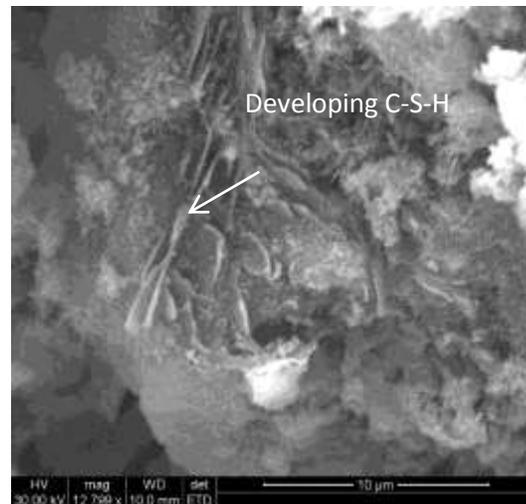
Figure 7: Total heat measured for control and MS admixed with cement pastes

3.5 Cement Pastes Micrographs

The scanning electron micrographs obtained from the cement pastes samples (control, CA 0.5, CA 1.0, CA 1.5, CA 2.0, MS 0.5, MS 1.0, MS 1.5 and MS 2.0) after a day of curing in water are as presented in Figure 8. The micrographs showed the samples as exfoliated pieces of materials and this agrees the observations of Jennings et al. [37]. The authors noted that within the early periods of hydration, the products formed are fibrous in nature and about less than 1% reaction takes place during induction period. Taylor [38] reported that between 3 hours of the start of hydration to about 24 hours, 30 % of cement would have reacted. The author further stated that the period is characterized by high evolution of heat and quick development of calcium silicate hydrates (C-S-H) and calcium hydroxide (CH) which is one of the earliest hydration products that is usually formed according to Hrbek et al. [39]. Ettringite formations can be observed in control CA 0.5, CA 1.0, CA 1.5, and MS 1.0. The morphologies of the samples at the early days of hydration is characteristic of what is expected as seen in Figure 8 and this agrees with what was reported by Stutzman [40]. Pockets of empty shells can be seen in all the micrographs shown in Figure 8 that can be ascribed to the hydration process. Scrivener [14] attributed the formation of separated hydrate shells after induction period to around 1 day to the development of amorphous substances on cement grains surfaces, which may hinder the deposit of C-S-H on the grains surfaces. The author further pointed out that cement grains that are less than 5 μm hydrate fully at this period which leads to empty shells during hydration. Taylor [38] noted that available spaces around 0.5 μm in width are most likely to be occupied with colloidal liquid, since the shells are reasonably permeable at this period there would be ionic migration through them. Taylor [38] further stated that the presence of these openings is an indication that the reaction progresses by both disintegration and precipitation. It is also noted from the micrographs that at 1 day that well-formed hydration products such as ettringite, C-S-H and CH can be seen in the Control, CA 0.5, CA 1.0, MS 0.5 and MS 1.0 pastes respectively. Whereas for CA 1.5, CA 2.0, MS 1.5 and MS 2.0 pastes the hydration products were not obvious. This may be an indication of the retarding effect of higher concentration of starch on hydration of cement.



Control day 1 (a)



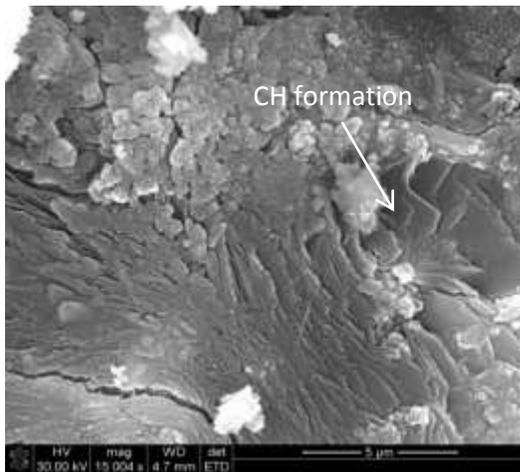
CA 0.5 day 1 (b)



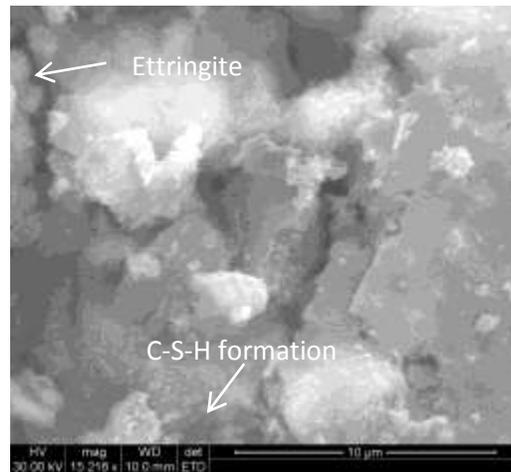
CA 1.0 day 1 (c)



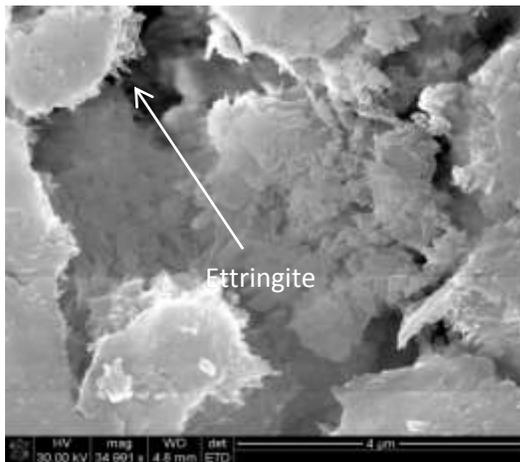
CA 1.5 day 1 (d)



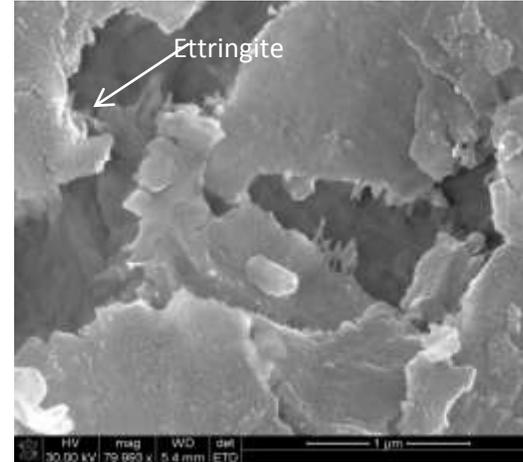
CA 2.0 day 1 (e)



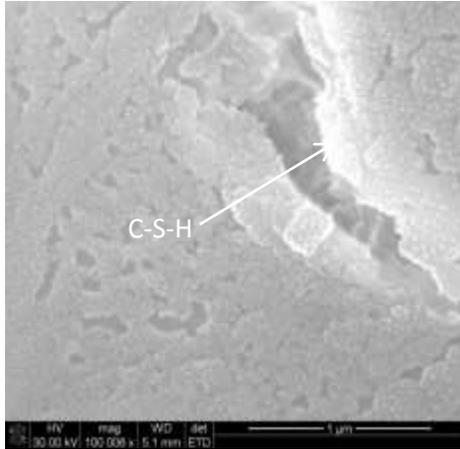
MS 0.5 day 1 (f)



MS 1.0 day 1 (g)



MS 1.5 day 1 (h)

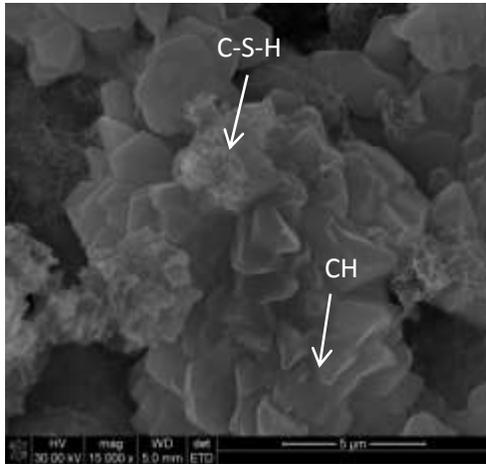


MS 2.0 day 1 (i)

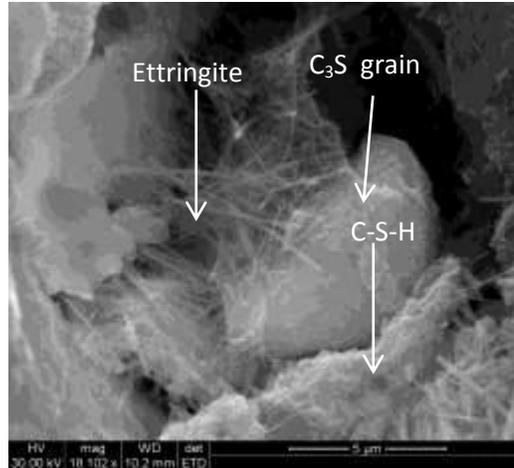
Figure 8: Micrographs of cement pastes with different starch concentrations after 1-day curing

The micrographs of the second day of hydration are presented in Figure 9. Figure 10(a) illustrates the micrograph of the control paste with CH platelets and C-S-H are quite distinct. The samples are less porous with the formation of more C-S-H gel to bind the CH crystals together. Ettringite and C-S-H were well observed in CA 0.5-day 2 micrograph (Figure 9), further hydration process is noticed as C-S-H gels are seen covering the faces of the cement grains and the ettringite and C-S-H formation around alite (C_3S) grain. The growth of gel (C-S-H) from within the surface of cement grains and development of long ettringite needles nucleating at the edge of the gel agrees with the reported findings in Taylor [38]. Figure 9(c) shows the growth of hydration products of CA 1.0. The C-S-H are seen on top of which CH crystals are well packed, with ettringite rods well pronounced. Figure 9(d) illustrates the growth pattern of CA 1.5 after two days of curing. The growth of the hydration products of CA 1.5 formed showing CH crystals. The micrograph of CA 2.0 is depicted by Figure 10(e), C-S-H can be clearly seen in the micrograph so also are ettringite rods and some CH crystals. MS 0.5 micrograph is shown in Figure 9(f), ettringite rods are clearly displayed with CH crystals. C-S-H are underneath the CH and are clearly shown.

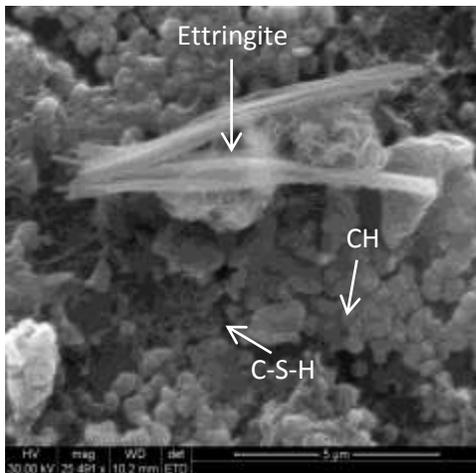
Figure 9(g) illustrates the micrograph of MS 1.0, The fibre-like C-S-H shown in this micrograph are more pronounced in shapes. MS 1.5 and MS 2.0 shown in Figure 9 illustrate that CH, C-S-H and ettringite are observed in the two micrographs. It is worthy to note that all the micrographs differ from one another. Generally, the C-S-H formed is a well-bonded web-like fine network of gel structure. Richardson and Groves [41] reported that the further hydration reaction and microstructural development occur after 24 hours even though at a slower rate, however, the core microstructural characteristics are sustained.



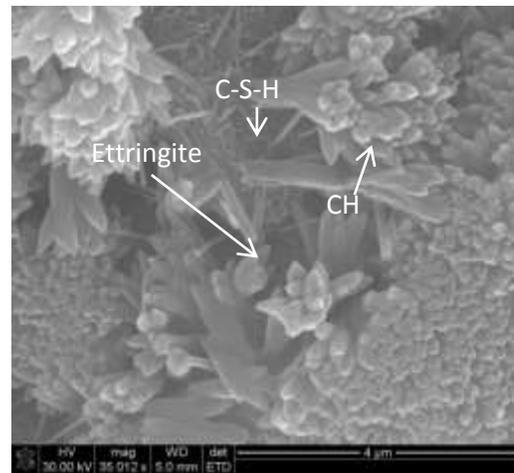
Control day 2(a)



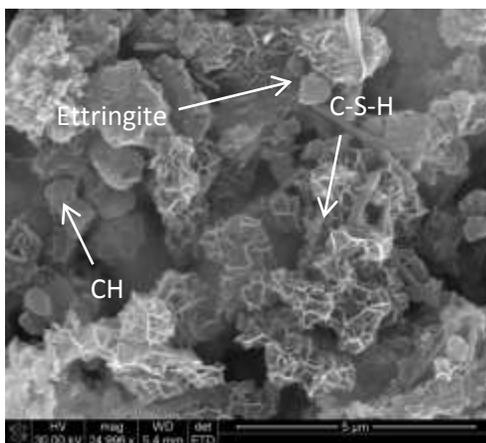
CA 0.5 day 2 (b)



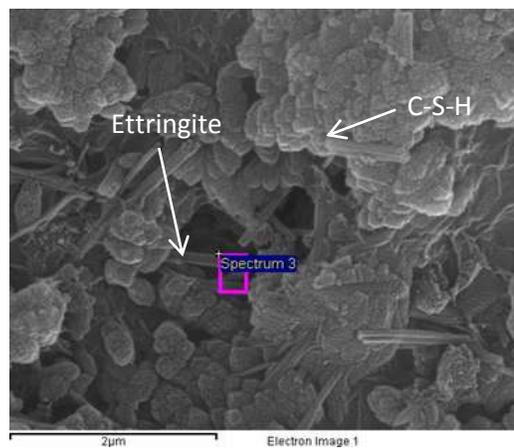
CA 1.0 day 2(c)



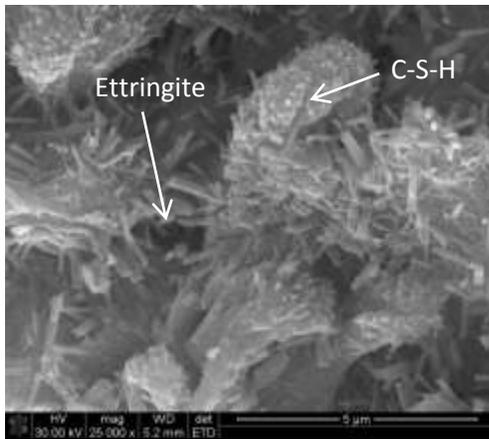
CA 1.5 day 2(d)



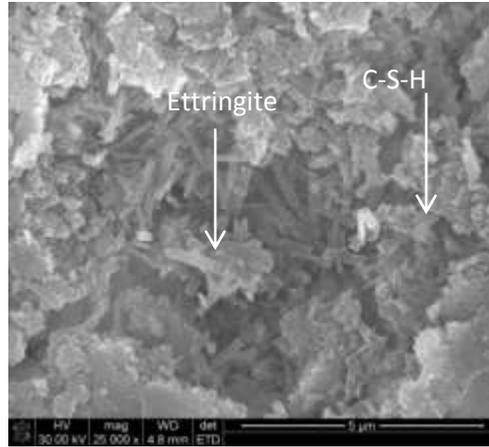
CA 2.0 day 2(e)



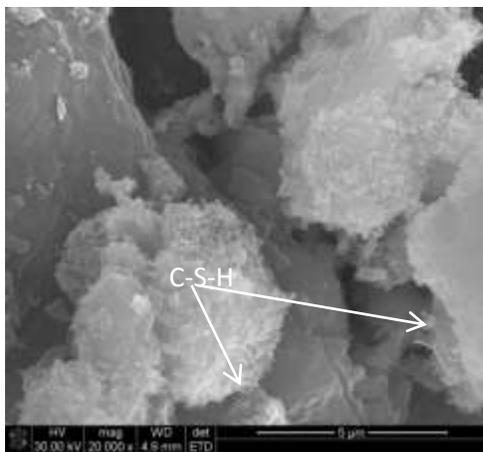
MS 0.5 day 2(f)



MS 1.0 day 2(g)



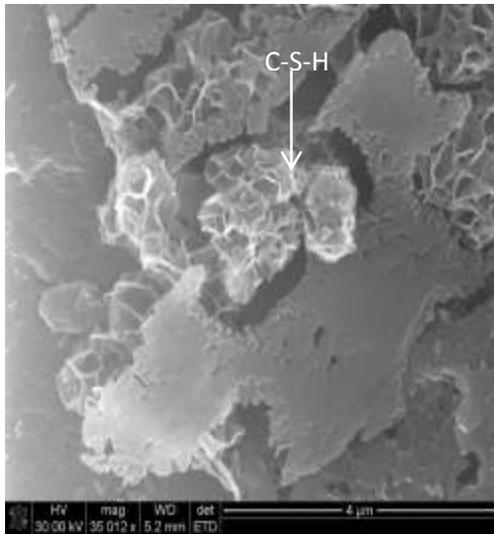
MS 1.5 day 2(h)



MS 2.0 day 2(i)

Figure 9: Micrographs of cement pastes with different starch concentrations after 2 days of curing.

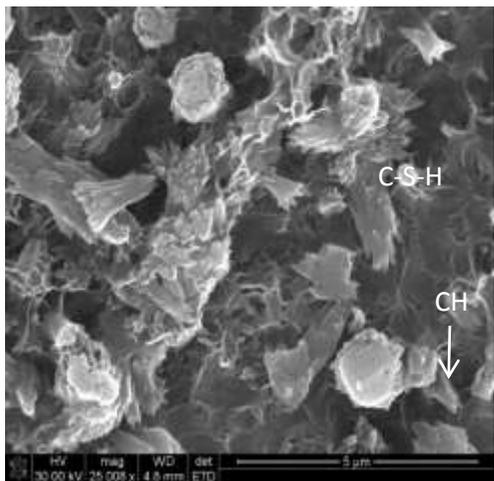
The morphologies of the pastes with different starch concentrations cured for 3 days are as shown in Figure 10. General observations of all the micrographs indicate a substantial departure from what are observed from Figures 8 and 9. The crystals are more fully formed; the growth characteristics of C-S-H takes the form of honeycomb-like having prolonged fibrous environment. This is consistent with previous findings of Viehland et al. [42], Scrivener [14] and Richardson [43]. It can be observed that ettringite formation is no longer seen as common in the micrographs of the 3 day cured pastes when compared with that of day-2 pastes, this is because the monosulphate crystals may have intermixed with C-S-H as hydration progresses with age as reported by Scrivener [14]. The structure of the micrographs show that the starches may have either been combined with C-S-H gel since it is also amorphous like starch or adsorbed onto the crystals surfaces, this is also what Luke and Luke [7] adduced to their investigation into the effect of sucrose on retardation of cement.



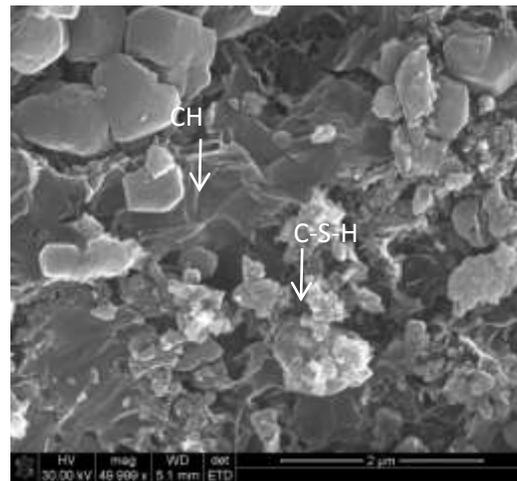
Control day 3



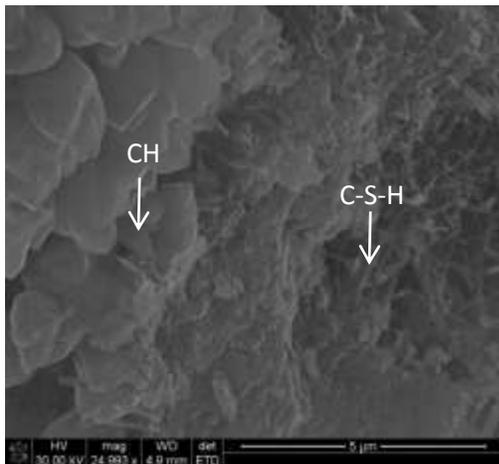
CA 0.5 day 3



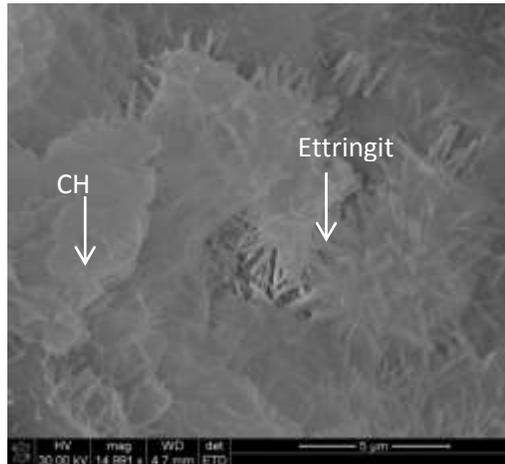
CA 1.0 day 3a



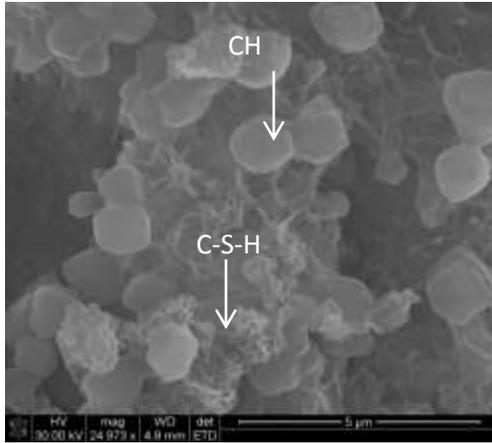
CA 1.5 day 3



CA 2.0 day 3



MS 0.5 day 3



MS 1.0 day 3



MS 1.5 day 3

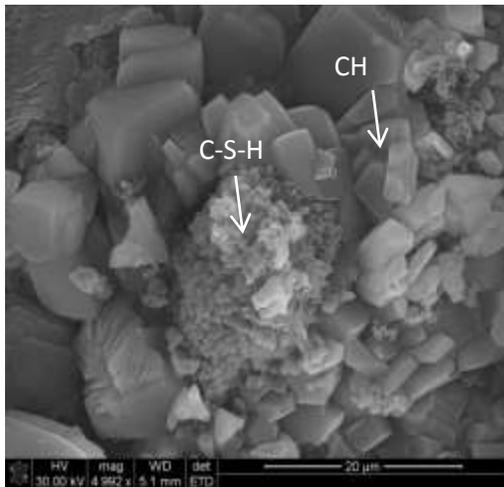


MS 2.0 day 3

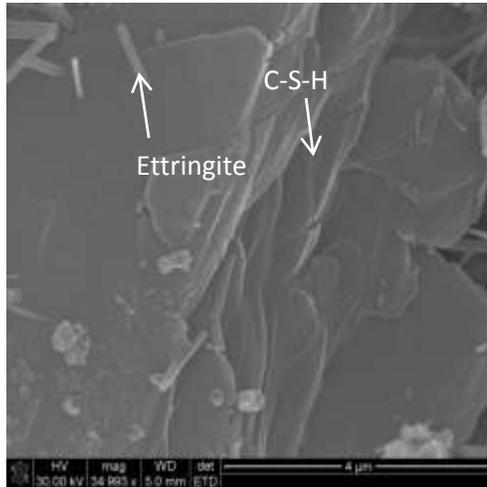
Figure 10: Micrographs of cement pastes with different starch concentrations after 3 days of curing.

Taylor [38] pointed out that as time goes on, the shells become less porous C-S-H is also deposited on their insides, any grains that is less than 5 μm tends to completely react at this stage. Tricalcium aluminate (C_3A) react with ettringite (Aft) inside the empty spaces (shells) to form monosulphate (AFm). Richardson and Groves [41] noted that the formation of Aft and AFm phases vary, it depends on the extent of hydration, the sulphate ratio and the structure of sulphate in cement among others. AFm is present in fully developed paste in the form of polygonal plates which may be confused with CH even though unstable and soon lose the crystallinity.

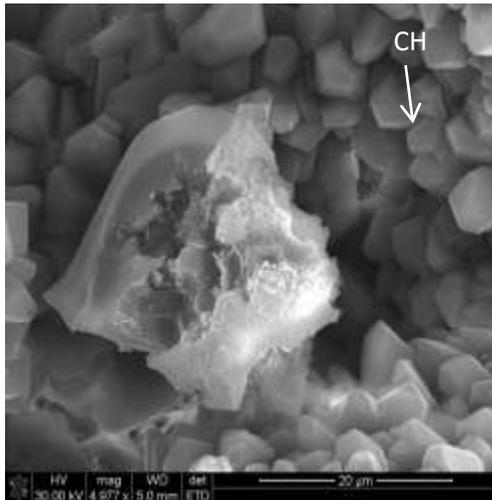
The morphologies of the paste samples with different starch concentrations cured for 7 days is as presented in Figure 11. Observations from all the micrographs revealed that the pores are filled up so also are the spaces between the shells. Well-formed CH crystals can be seen in all the micrographs. It is to be noted that the micrographs were taken using different magnifications; this was done in order to focus on areas of interest that may not be very obvious at lower magnification. Taylor [38] stated that shells are about 8 μm in thickness at this stage and are filled mainly with the deposited materials in their surfaces on the inside (e.g. MS 1.0 day 7 (g)).



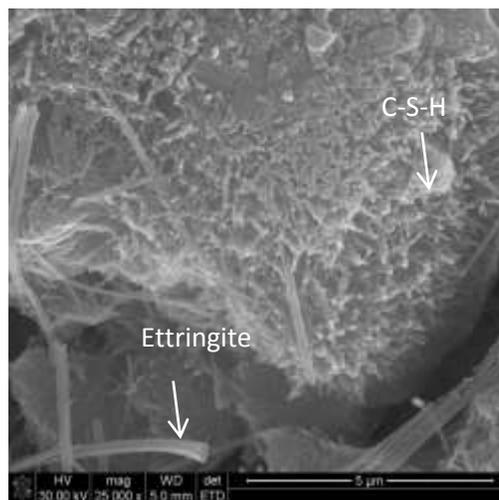
Control day 7 (a)



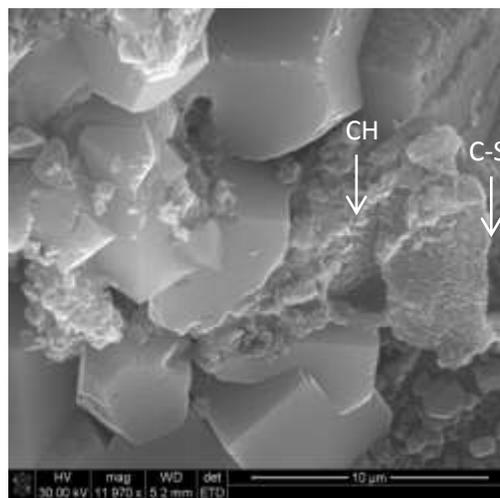
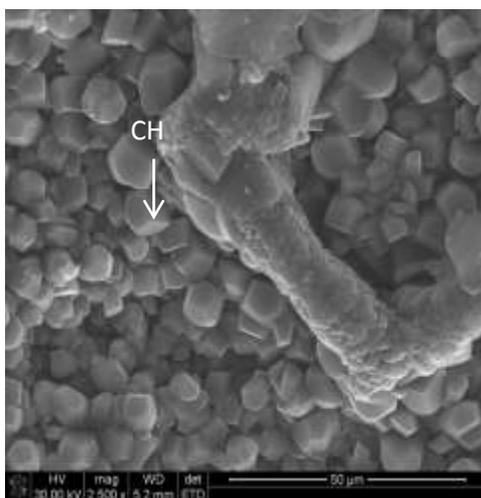
CA 0.5 day 7 (b)



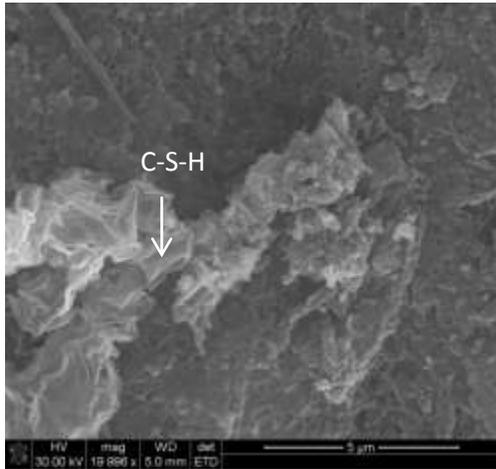
CA 1.0 day 7 (c)



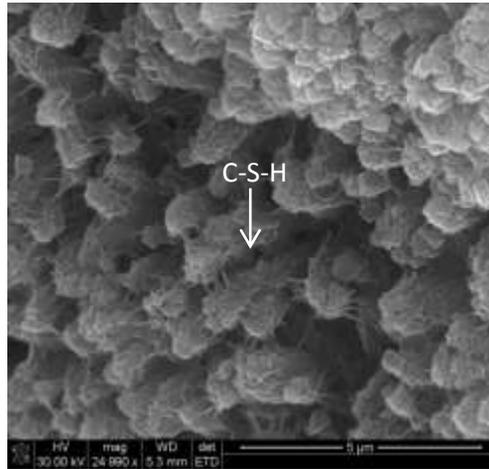
CA 1.5 day 7 (d)



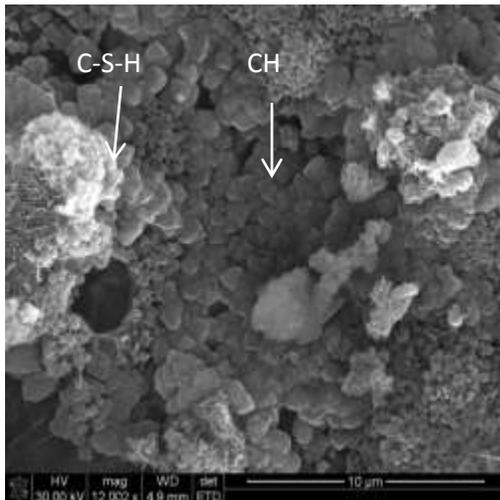
CA 2.0-day 7a (e)



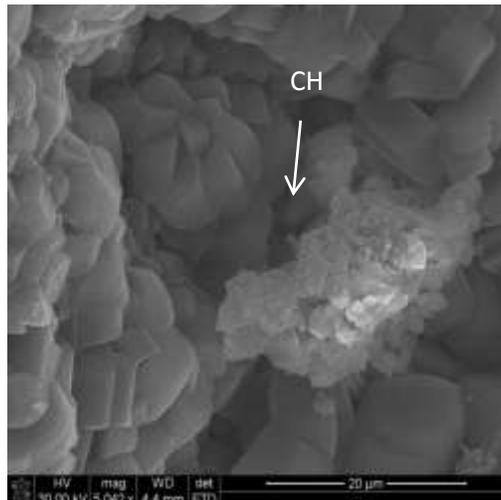
CA 2.0 day 7b (e)



MS 0.5 day 7 (f)



MS 1.0 day 7 (g)

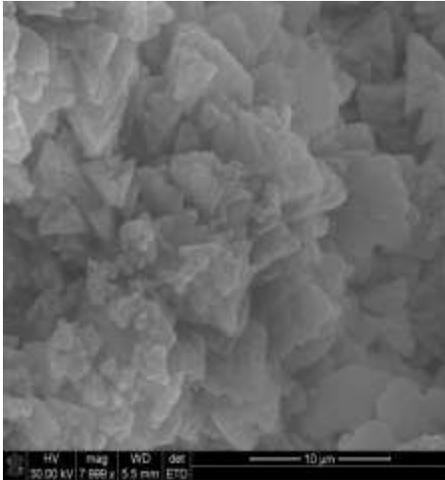


MS 1.5 day 7 (h)

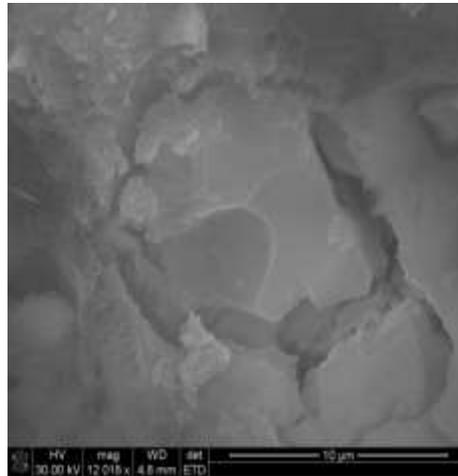
MS 2.0 day 7 (j)

Figure 11: Micrographs of cement pastes with different starch concentrations after 7 days of curing.

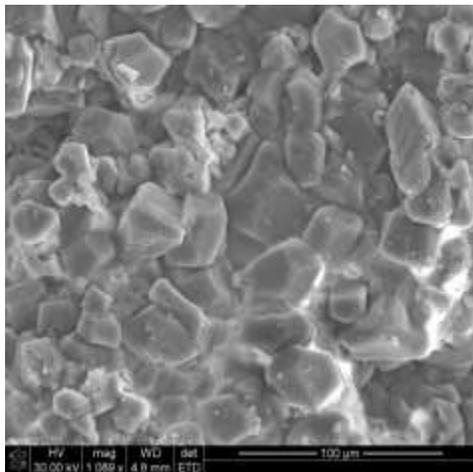
The author further pointed out that at this stage the quantity of sulphate would reduce drastically because of the reaction of aluminate to form AFm and Aft phase is translated to AFm. Though Afm as it was said earlier may have intermixed with C-S-H and its polygonal plate-like as noted by Matschei et al., [44] structure may be mistaken for CH though not stable. The observations of the micrographs at seven days in Figure 11 show that ettringite needles are no longer common. The most noticeable compounds are the CH and C-S-H in all the micrographs. Taylor [38] illustrated that the morphology of C-S-H formed at this stage to be foil-like and this is consistent with what is obtainable in all the micrographs shown in Figure 11. One thing about the morphologies at this stage is that empty spaces are filled up and this does not allow for the development of any large interconnected capillary pores which improves durability performance of the cementitious systems according to Richardson [43] and Wang et al. [45].



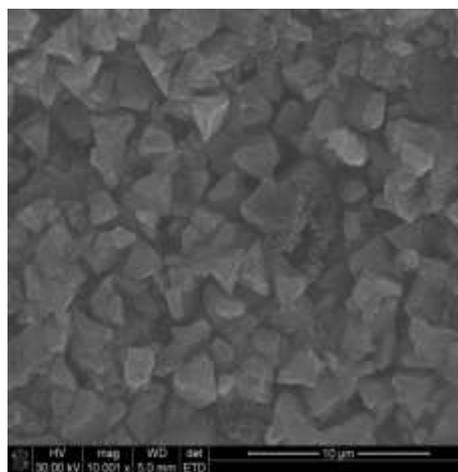
Control day 28



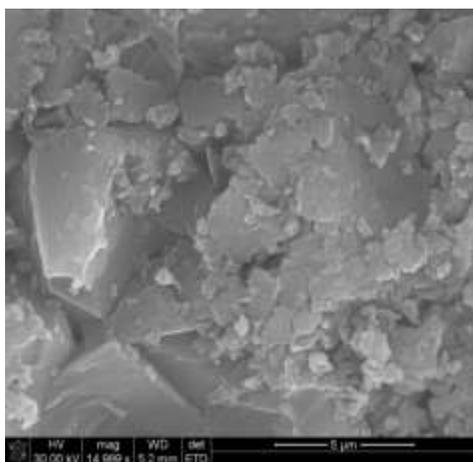
CA 0.5 day 28a



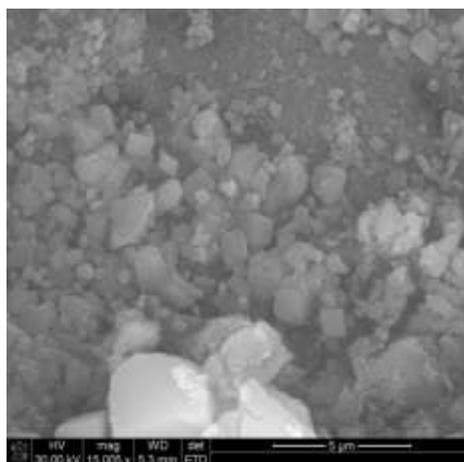
CA 0.5 day 28b



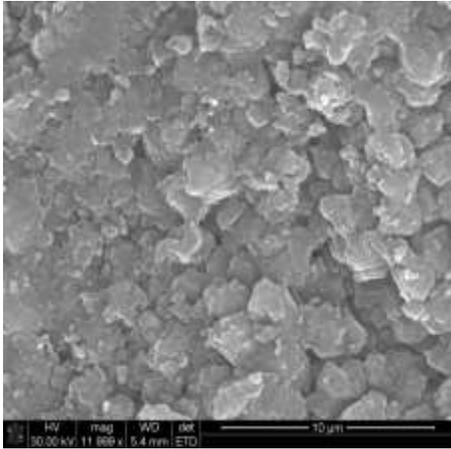
CA 1.0 day 28



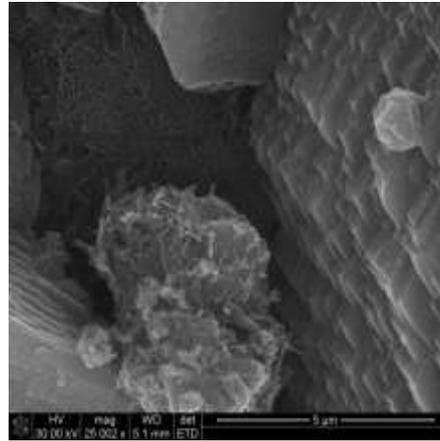
CA 1.5 day 28a



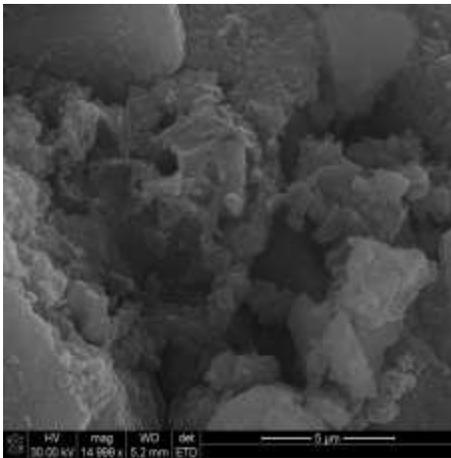
CA 1.5 day 28b



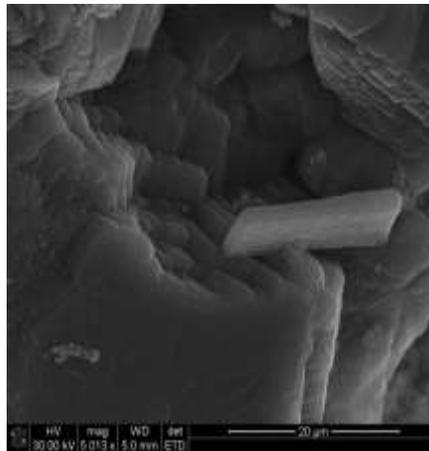
CA 2.0 day 28



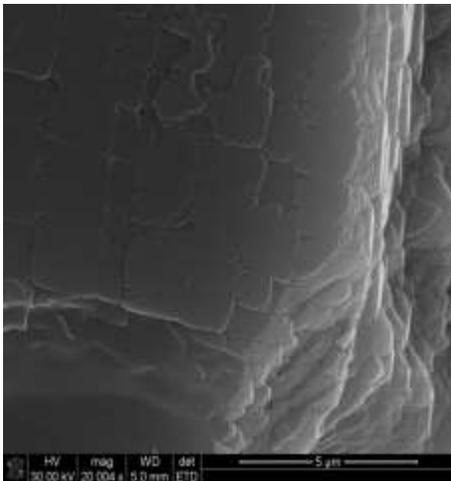
MS 0.5 day 28



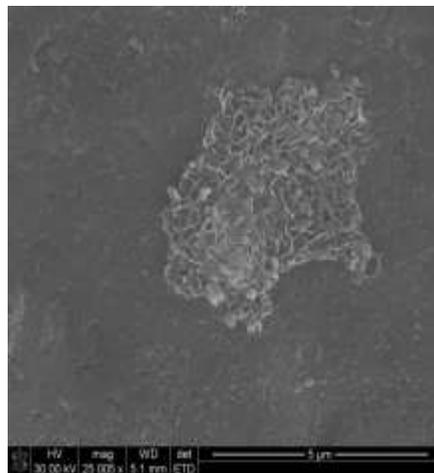
MS 1.0 day 28



MS 1.5 day 28a



MS 1.5 day 28b



MS 2.0 day 28

Figure 12: Micrographs of cement pastes with different starch concentrations after 28 days of curing.

The morphologies of the starch modified cement pastes with different starch concentrations after 28 days of curing are as presented in Figure 12. Aft needles were no longer seen in any of the observed micrographs even though Taylor [38] pointed out that it is still possible to notice some Aft in old cement pastes if their precipitation had taken place outside the shells.

3.7 Results of FT-IR Spectroscopy

The result of FT-IR spectroscopy which was used to identify and validate characterization of compounds in the starch (cassava and maize) admixed cementitious systems with the use of vibrational technique are as presented in Figures 13 and 14. The major observations noted in the results (see Figures 13 and 14) are:

- i. The effects of the additions of 0.5, 1.0, 1.5 and 2.0 % by weight of cement of both cassava and maize starches on the cementitious systems are very similar;
- ii. The results obtained with the starch admixed cementitious system of 0.5% and 1.0% are similar.

The summary of the results of the hydrated infrared bands of starch (cassava and maize) admixed cementitious systems is as presented in Table 2. The characteristic absorption bands of portlandite ($3630 - 3673 \text{ cm}^{-1}$) were observed for all the mixes, it is formed as silicate phases in the cement dissolve with increasing intensity as hydration continues [46], having residual water at $3296 - 3489 \text{ cm}^{-1}$. The IR bands ($2982 - 2995 \text{ cm}^{-1}$) are assigned hexagonal hydrates ν_3 because of the presence of water in gypsum [2, 47] and for the same band in starch admixed pastes it was assigned to C-H. Ylmén et. al., [47] pointed out that dissociation of some of the crystallized water in the gypsum takes place because of heat generated when water is added to cement. The sulphates, aluminates and ferrites in the cement react to form AFt phase. Further reaction of this phase with aluminates and ferrites leads to the formation of AFm phase.

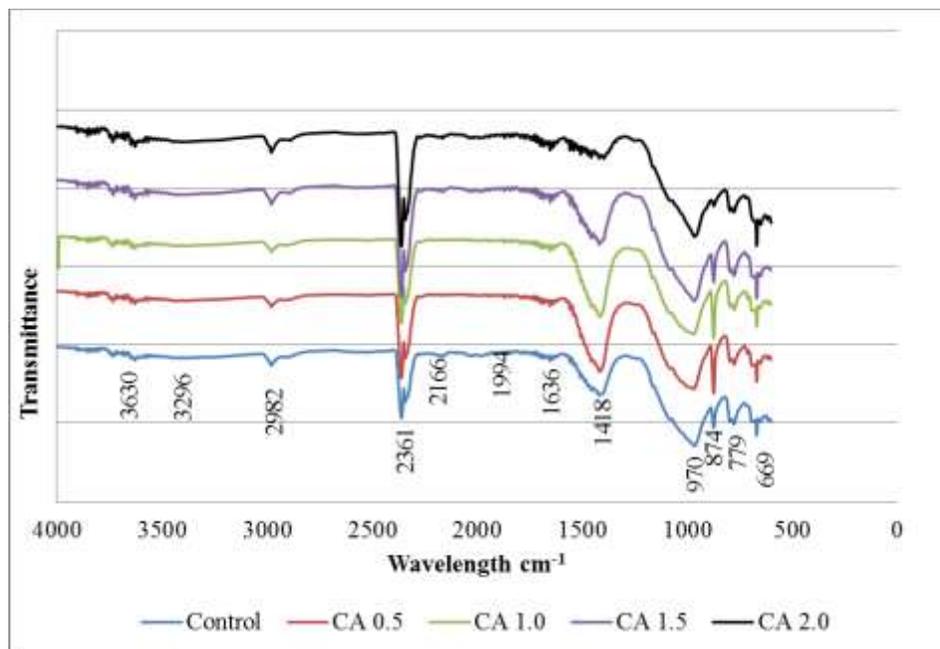


Figure 13: FTIR for Control and CA admixed cement pastes

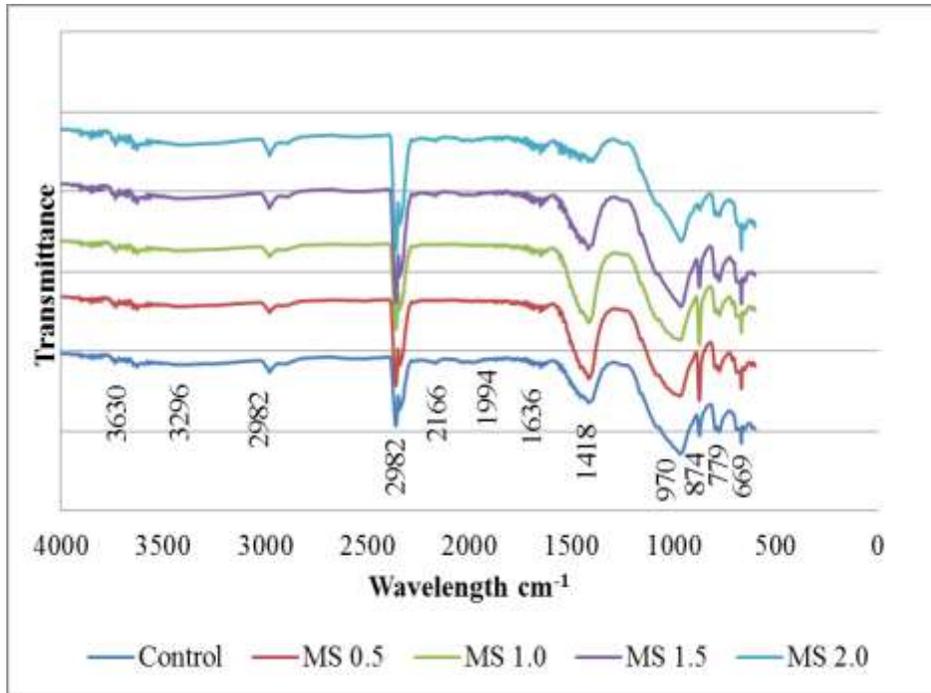


Figure 14: FTIR for Control and MS admixed cement pastes

Table 2: Observed transmittance peaks in Figures 13 to 14

Possible assignment	IR band (cm ⁻¹)	Control 0	CA & MS starch			
			0.5%	1%	1.5 %	2.0 %
O-H; Portlandite	3630 - 3673	x	x	x	x	x
OH residual water	3296 - 3489	x	x	x	x	x
C-H: Hexagonal hydrates	2979 – 2982	x	x	x	x	x
Isocyanate	2361	x	x	x	x	x
H ₂ O in Sulphates	1636 - 1652	x	x	x	x	x
OH; CO ₃ ²⁻	1358 - 1420	x	x	x	x	x
Si-O; Silicates, CSH	950-1000	x	x	x	x	x
Si-O; C ₃ S	800 - 900	x	x	x	x	x
Si-O; C ₂ S	775 - 779	x	x	x	x	x
Si-O; Silica	669	x	x	x	x	x

* indicates that the compound is present

There is the probability of impurity in the cement as shown with the infrared band at 2361 cm^{-1} which may be associated with isocyanate [48, 46], it increases with the increase in starch concentrations in the cementitious systems as seen in Figures 13 and 14. This impurity may have been responsible for the initial retardation of the hydration process of the starch admixed concretes as impurity does retard hydration process. It also confirms the retarding behaviour of the starches during the hydration process as seen in Section 3.3. Water in sulphates is associated with ettringite formation is depicted by 1636 cm^{-1} IR bands [49, 47].

The peaks (Figures 14 and 15) at $1358 - 1420\text{ cm}^{-1}$ are assigned to calcium carbonate in agreement with Carrasco et. al., [49] and according to Heikal et. al., [50]. It occurs because of carbonation of hydration products which reduces as the hydration proceeds and time of curing continues. however, it is observed that at IR bands $1358 - 1420\text{ cm}^{-1}$ (Figures 13 and 14). The intensity of calcium carbonate peaks decreases with percentage increase in starch content in the mixes, this may be due to reaction with OH identified in starch at this band, also calcite reacts with aluminate to form some compounds of less crystalline phases such as carboxyaluminate [47].

The characteristic peak intensity around $950 - 1000\text{ cm}^{-1}$ is associated with calcium silicate hydrates (C-S-H), the intensity increases as the hydration of cementitious system continues. It occurs as alite (C_3S) in the system dissolves and the silica in the system at the same time polymerizes. Continuation of hydration process will lead to reduction in the quantity of available C_3S in the system and subsequent progressive decrease in the intensity of the peak associated with C_3S in $800 - 900\text{ cm}^{-1}$ as illustrated by Heikal et al., [51] and Ylmén et al., [47]. The peak spectrum at $775 - 779\text{ cm}^{-1}$ band is probably associated with belite (C_2S) due to the stretching Si-O bond of the silicon tetrahedron [46, 48] with bending vibrations absorption band at 669.29 cm^{-1} .

4 CONCLUSIONS

- i. It can be concluded from this study that starch extracted from cassava and maize was found to prolong setting time of and delayed peak heat rate of hydration of cement, the delay in the degree of hydration however depends on the concentration of the starch in the concrete. Cassava starch was found to retard hydration a little longer than maize starch. This also confirmed the results of the initial and final setting times as presented in Section 3.1
- ii. SEM results show the micrographs of the development of hydration products at different stages over a 28-day period of the hydration process for all the cementitious systems. The early micrographs showed a delayed formation of hydration products especially in the early days between 1-3 days for CA 1.5, CA 2.0, MS 1.5 and MS 2.0.
- iii. The FTIR tests particularly gives information on the wavelength at which to expect a slowdown of the hydration process at $2360 - 2361\text{ (cm}^{-1}\text{)}$ wavelengths. It illustrates that the greater the concentration of the starch in concrete the higher the peak, which is an indication of greater retarding effect of starch on the hydration process of cement. This confirms the result obtained from Sections 3.3 and 3.4 that increased concentration of starch has greater retarding effect peak heat rate hydration of the cementitious system. The investigated starch can

therefore, be used in concrete casting hot climate in as admixture to delay the hydration peak to give adequate time placement and compaction.

5 RECOMMENDATIONS

The performance of starch during hydration have been demonstrated in the paper, however, its use will be better within the range of 1% addition to concrete in view of the initial and final setting times recorded for starch concentrations of 1.5% and 2.0% especially for cassava. Concretes produced with 1.5% and 2.0% starch additions were more and stiffer and may require the use of superplasticizer.

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