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Properties of corn cob ash and effect on hydration kinetics in PC-blended cementitious systems

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Abstract
The study investigates the effects of the properties of calcined corn cob ash on the hydration kinetics of Portland cement (PC). The corn cob ashes were used at PC replacement levels of 15% and 30%. The materials were characterised for oxide composition and amorphous content using XRF and XRD respectively. The reactivity of the corn cob ashes was assessed using both the R^3 Test (ASTM C1897-20) and the strength activity index (SAI). The hydration kinetics of the corn cob ashes was assessed using isothermal calorimetry at 20 °C with measurements taken up to 48 h. The results show that the corn cob ashes produced at the two temperatures are largely crystalline, showing little pozzolanicity even though the SAI indicated otherwise. Partial replacement of PC with corn cob ash affected the evolution of heat of hydration of PC, prolonging the induction phase and delaying the evolution of the main heat peak.

Keywords Corn cob ash, Calorimetry, Hydration kinetics, Reactivity, Strength activity index (SAI)

1 Introduction

The need to reduce the amount of Portland cement clinker used in concrete due to its negative effect on the environment has resulted in a shift of focus from plain Portland cement to the investigation of new sources of supplementary cementitious materials (SCMs), sometimes referred to as non-conventional cementitious materials (NCCMs). These new sources of SCMs being investigated are from waste materials [37] and some from naturally occurring materials [3] with potential material properties for utilisation as partial replacement for plain Portland cement (PC). For naturally occurring materials, the material properties are fairly uniform and partly dependent on the geological formation process such as volcanicity, while waste materials especially those emanating from agricultural crops have variable composition which is largely dependent on the biomass type and processing method [13]. It is therefore important that such non-conventional materials are assessed for viability as SCMs.

The validation of NCCMs requires investigation into material properties and performance in cementitious systems to assess material behaviour and compatibility with plain PC. This is essential in the classification and utilisation of new materials as SCM. Oxide composition of an NCCM especially the CaO, SiO_2 and Al_2O_3 is one important consideration being used to identify a potential SCM and to further understand its reaction mechanism and interaction with plain PC. Previous studies on SCMs obtained from agricultural wastes such as rice husk ash, corn cob ash and sugarcane bagasse ash have shown positive results in this regard while their potential use have also been reported [2, 6, 14, 33, 38].

Much emphasis has often been placed in past studies on the impact of agro-based SCMs on the on the strength development of concrete [1, 2, 28]. However, the sometimes lower strength and longer curing period reported compared to plain Portland cement concrete requires further investigation as there are other factors which may assist in better classification and development of such materials for use. Understanding the impact of NCCMs on the hydration kinetics of PC is considered important for further development, classification and, ultimately, utilisation as partial replacement for Portland cement in cementitious systems. The loss on ignition (LOI), an indicator of the unburnt carbon content is also an important property which can be used as a quality measure but is known to be affected by the method of calcination and ash treatment thereafter. It has been reported to affect water demand and hence workability in cementitious systems [10, 19]. Furthermore, these properties can aid in understanding their physical and/or chemical contribution to strength and durability performance when used in cementitious systems.

Corn cob is an agricultural waste obtained from processing harvested maize (*Zea mays*) and is common in sub-Saharan Africa where maize is a staple food. Corn cob constitutes between 18% and 20% by volume of the total bio-waste generated from processing harvested maize [12], [24]. It is usually disposed of in open fields where it is left to decay under the influence of natural agents, or burnt in heaps depending on the method of harvesting employed, while in some local setting a little fraction may be used for energy production. Improper disposal of these wastes has a negative effect on the living component of the environment, hence the need for proper investigation into their properties to aid proper recycling and valorisation. This paper studied the hydration kinetics of corn cob ash as a partial substitute for plain PC with a view to understand its reaction mechanism as a SCM in cementitious systems and aid its classification and value addition in construction application. Understanding the reaction mechanism is crucial to understanding the compatibility with plain PC, enhance further development and/or assess the extent of use in cementitious systems. Subsequently, this information can assist in understanding the low compressive strength inherent of concrete containing corn cob ash.

2 Experimental set-up

2.1 Materials

Corn cob ashes (CCA) obtained from two preparation processes were used as partial replacements for plain Portland cement, PC (CEM I 52.5R). In the first preparation process, corn cobs were pyrolysed by burning into carbon black and then milled to powder. The milled powder was further calcined in a furnace at 800 °C for at least two hours to reduce the carbon black to ash. The ash obtained through this method is labelled C-800. In the second preparation process corn cobs were calcined in a drum furnace. The calcination temperature was not controlled but was monitored using a temperature probe. The stable temperature in the furnace was about 700 °C. The CCA obtained through this method is labelled C-700. The choice of the calcination method and temperature was dictated by the available means during the time of carrying out the study and in a way typifies the limitation and challenges of preparing agro-based ashes in the laboratory. The ashes obtained from the two processes were all subjected to gradual cooling at ambient temperature before collection. The collected ash was milled in a laboratory vibratory disc mill and the finesses and particle size measured – see Table 1 which presents selected geometric and physical properties of the various SCMs used in the study. Adopting the two ash preparation processes facilitated the comparison of the impact of processing method on material characteristics and subsequently on the performance of the ashes in cementitious systems. The two ashes C-700 and C-800 were used as SCMs separately to replace PC by mass at two replacement levels of 15% and 30% to obtain blended cements C-700-15, C-700-30, C-800-15 and C-800-30. The commonly used replacement level for fly ash in South Africa is 30% for strength and durability requirements [18]. The replacement levels were chosen to enable comparison of effects of the SCMs at low and moderate substitution levels which allows distinction of the effects of the SCMs in cementitious systems.

2.2 Material characterisation

Particle size distribution of the ashes was determined through laser diffraction method using Anton Paar PSA 1090 particle size analyser. The oxide composition of the ashes was determined through X-ray florescence using a PANalytical Axios X-ray spectrometer. The phase analysis of the ashes was determined through x-ray diffraction method

Table 1 Oxide composition and selected properties of SCMs

Oxide[a]/phase/property	**Percentage (%)**			
	C-700	**C-800**	**Fly ash**	**CEM I 52.5R**
SiO_2	59.37	63.68	56.01	19.57
CaO	1.26	2.37	5.00	62.57
Na_2O	0.16	0.24	< 0.01	0.00
K_2O	15.83	11.22	0.77	0.45
Al_2O_3	2.79	4.42	31.74	4.93
Fe_2O_3	2.62	4.05	3.31	2.64
MnO	0.07	0.11	0.01	0.37
MgO	1.38	2.07	1.22	2.06
TiO_2	0.41	0.50	1.59	0.35
P_2O_5	1.76	3.20	0.56	0.10
Cr_2O_7	0.07	0.09	0.04	0.03
LOI	13.19	6.76	0.81	3.60
Amorphous content[b]	1.90	2.40	57.5	–
D_{10} (μm)	1.63	1.06	0.15	30.11
D_{50} (μm)	12.41	6.11	1.17	38.72
D_{90} (μm)	54.93	24.50	3.37	225.72
Mean size (μm)[c]	22.00	9.96	1.38	95.09
Fineness (BET, m^2/g)	3.12	2.75	2.22	2.38

[a] X-ray fluorescence (XRF) analysis

[b] X-ray diffraction (XRD) analysis

[c] Volume-weighted mean particle size

using PANalytical X'Pert Pro diffractometer with X'Celerator detector and fixed slits with Fe-filtered Co-Kα radiation while the quantification of the phases was done using the Rietveld method. The specific surface area of the ashes was determined using the Bruner-Emmett-Teller method with a gas adsorption analyser, Nova 800 BET. The morphological characterisation of the ashes was done through scanning electron microscopy using a Tescan Vega3 microscope using secondary electron mode.

2.3 R^3 Test

The R^3 reactivity test using the bound water approach was used to assess the relative pozzolanic reactivity of the corn cob ashes following ASTM C1897-20 [4]. Paste samples prepared using each of the CCA were tested for reactivity in a simulated alkaline environment. The paste is prepared by mixing CCA, $Ca(OH)_2$, $CaCO_3$ with 54 g of a potassium-based solution. 10 g of CCA, 30 g of $Ca(OH)_2$ and 5 g of $CaCO_3$ are mixed in the ratio 1:3:0.5 by mass while the potassium-based solution is made by mixing 4.0 g of KOH and 20 g of K_2SO_4 in 1.0 L of deionised water. Immediately after placing in the moulds, the paste samples were placed in an oven maintained at 50 ± 2 °C for 7 days. It is important to note that the curing temperature used was higher than that recommended in ASTM C 1897-20 of 40 °C. However, previous studies have shown that using 40 °C does not affect the results and only acts to accelerate the chemical reactions [5]. At the end of the 7 days curing at 50 ± 2 °C, some paste samples had hardened while other had not. The hardened paste samples were crushed into small pieces (particle size ~ 2.0 mm) in a mortar and pestle and then oven-dried at 50 ± 2 °C for 24 h prior to testing. The paste samples that had not hardened sufficiently were broken into small pieces by hand and oven-dried at 50 ± 2 °C for 24 h prior to testing. The bound water content was thereafter determined by exposing the small particle size paste samples to temperature at 350 ± 10 °C while the mass loss thereof reported as the bound water for the temperature range 50 to 350 °C.

2.4 Isothermal calorimetry

Isothermal calorimetry at a constant temperature of 20 °C using an ICal 2000 H calorimeter was used to assess the heat of hydration characteristics of the blended cements C-700-15, C-700-30, C-800-15 and C-800-30. Paste samples for isothermal calorimetry were prepared by mixing 30 g of each of the PC/CCA blended cements with water using a water to powder ratio of 0.40. For reference purposes, companion samples were made by replacing CCA in each mix with either andesite crusher sand ($D_{10} = 1.75$, $D_{50} = 13.70$, $D_{90} = 55.10$, volume-weighted mean particle size = 23.19 μm) or fly ash. Andesite crusher sand was used as an inert material to assess the effects of the corn cob ashes on the hydration of PC hydration while fly ash which is a known pozzolanic material was used to assess the degree of pozzolanicity of the corn cob ashes, if any. The heat flow during the isothermal calorimetry was monitored for up to 48 h.

2.5 Strength tests

50 mm mortar cube specimens were cast for compressive strength testing after 28, 56 and 90 days curing in water at 23 ± 2 °C. The mix proportioning of BS EN 196:1 was adopted except that quartz sand was used in lieu of standard sand. A sand-to-cement ratio of 3:1 and water-to-powder ratio of 0.50 was used.

3 Results and discussion

3.1 Physical and chemical properties of the corn cob ashes

3.1.1 Oxide composition

The oxide composition of the ashes presented in Table 1 shows that both corn cob ashes C-700 and C-800 have high silica content ranging from 59 to 64%. ASTM C618 specifies a combined SiO_2, Al_2O_3 and Fe_2O_3 content of at least 70% for Class F fly ash and natural pozzolans and this is often used by extension for siliceous and/or alumina-siliceous materials. Only the corn cob ash C-800 meets this requirement.

It is also important to note that both corn cob ashes C-700 and C-800 have significantly high K_2O contents of, respectively, 16 and 11% compared to 0.8% for fly ash. The high K_2O contents is linked to the use of plant fertilizers with high potassium contents that are absorbed and stored in the corn cob. The high K_2O content signifies a likely fusion with silicate compounds in the ash which can be attributed to the high thermodynamic affinity of silicates for alkali earth oxides [8]. The presence of orthoclase in the corn cob ashes further substantiates this. Comparison with previous studies on corn cob ash showed that the K_2O content of the ash is generally high at about 5% and above [2, 28, 29, 34].

3.1.2 Loss on ignition

The results also show that the loss on ignition (LOI) is higher in C-700 ash than in C-800 ash, an indication that calcination in a controlled environment reduces the unburnt carbon content and other ignitable materials present in the corn cob ash. The presence of unburnt carbon signifies incomplete combustion process or reduced access to oxygen during the calcination process, this further means that there is a need to modify the calcination set-up to allow more oxygen flow in addition to reducing the particle size of the feedstock. Similar results have been reported by Memon and Khan [28] with an associated increase in water demand linked to the porosity of unburnt carbon particles. The presence of unburnt carbon has been associated with increased water demand, increased electrical conductivity and dark coloured concrete for fly ash with a high carbon content [19]. This could have contributed to the water demand of CCA blends compared to fly ash and plain PC as noted during the course of the experiment and this is likely due to the adsorption of free water at the surfaces of the unburnt carbon which tends to reduce workability.

3.1.3 Reactive phase content and morphology of the ashes

The reactive phase content (XRD) results presented in Table 1 show that both corn cob ashes C-700 and C-800 are largely crystalline; compared to fly ash which has an amorphous content of 58%, both corn cob ashes have very low amorphous contents of, respectively, 1.9 and 2.4%. It is clear that the calcination process employed in this study (which typify commonly used methods as obtained in literature) needs to be modified in order to produce the desirable high amorphous ash content that is typical of pozzolanic materials [32]. This may require understanding the dynamics of combustion in air as it pertains to the calcination of large quantities of lignocellulosic material (i.e. corn cobs) as a means of reducing the high calcination temperature while producing ash with low carbon content. Although, some studies have considered using extended calcination periods and varying the rate of cooling for sewage sludge [22]. This may not necessarily work for lignocellulosic materials due to their low melting point which can contribute to issue of slagging [17, 27] Data on the amorphous content of corn cob ashes in past studies could not be found in published literature for further comparison especially with respect to the contribution of calcination temperature on the reactive phase content of the corn cob ash.

The SEM micrographs presented in Fig. 1 show that both C-700 and C-800 have agglomerated non-uniformly shaped, rough surfaced particles compared to single spherical smooth surfaced particles of fly ash. The agglomeration of the CCA particles likely contributes to the coarseness of the particles and resulting in a lower surface area compared to fly ash. However, the smoothness or roughness of the surfaces of the particles contributes to the differences in their water demand when used alongside plain PC in cementitious systems. The degree of coarseness is somewhat uniform in both C-700 and C-800.

3.1.4 Particle fineness

The fineness of the particles of the ashes compared to plain PC is presented in Table 1. Considering the D_{50} and D_{90} of the CCAs, C-800 can be said to be twice as fine as C-700 with, respectively, 50% and 90% of the particles being finer than 6.11 μm and 24.50 μm compared to, respectively, 12.41 μm and 54.93 μm of C-700. The particles of C-700 and C-800 were coarser than those of fly ash while the particles of the CCAs and fly ash were finer than those of CEM I. The fineness of the ashes compared to that of CEM I has an

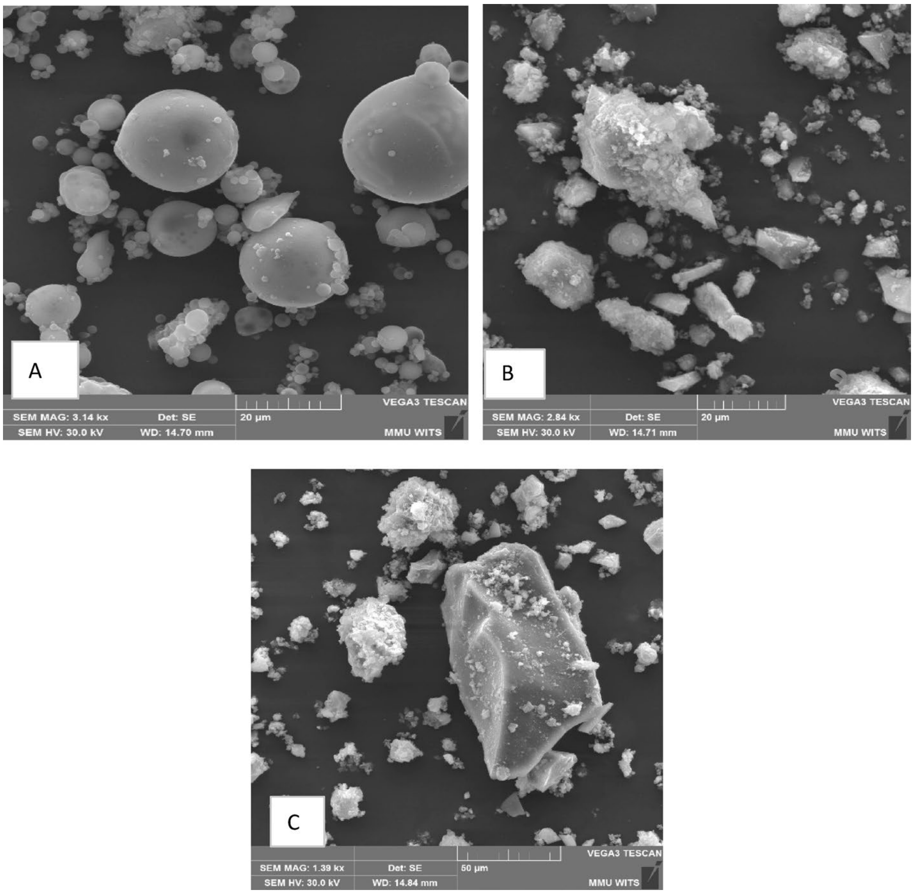

Fig. 1 SEM micrographs of Fly ash (**A**), C-800 (**B**) and C-700 (**C**) particles

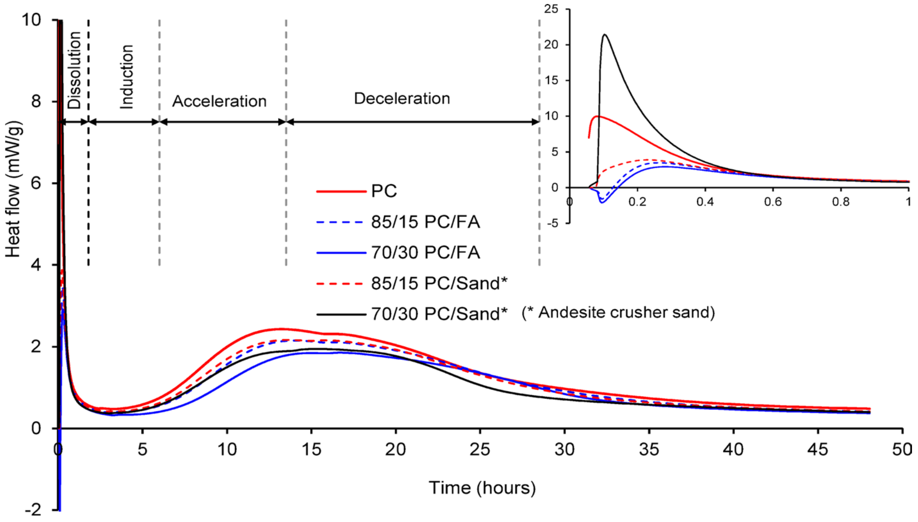

Fig. 2 Comparison of heat flow curves for plain PC, PC/FA and PC/Sand

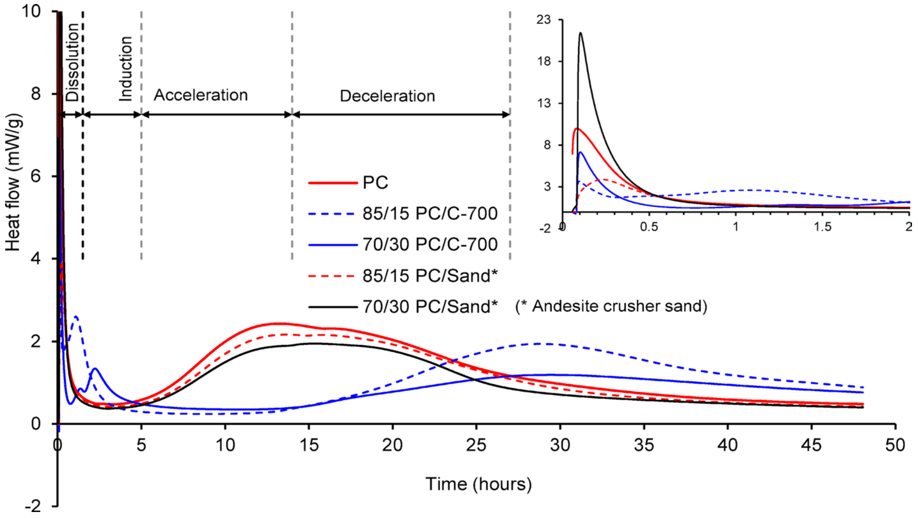

Fig. 3 Comparison of heat flow curves for PC, PC/C-700 and PC/Sand

effect on their filler behaviour as they can effectively fill the interparticle spaces in CEM I, thus having an influence on properties of cementitious systems especially compressive strength [11]. The specific surface areas of both C-700 and C-800 are larger than those for fly ash and this partly explain their increased water demand. The higher specific surface area of CCA compared to fly ash systems is envisaged to be as a result of agglomeration of the particles as well as the rough surfaces compared to fly ash given that fly ash is finer. Thus the higher specific surface area should not be taken as finer than fly ash as the SEM micrograph showed that on the average, fly ash particles are finer and more uniform than those of either C-700 or C-800.

3.2 Calorimetric results

The 48-hour isothermal heat flow curves of the corn cob ashes are presented in Figs. 2, 3 and 4. The measurement duration was sufficient to capture the dissolution, induction, acceleration and deceleration heat flow phases [16]. It is clear from Fig. 2 that the slight

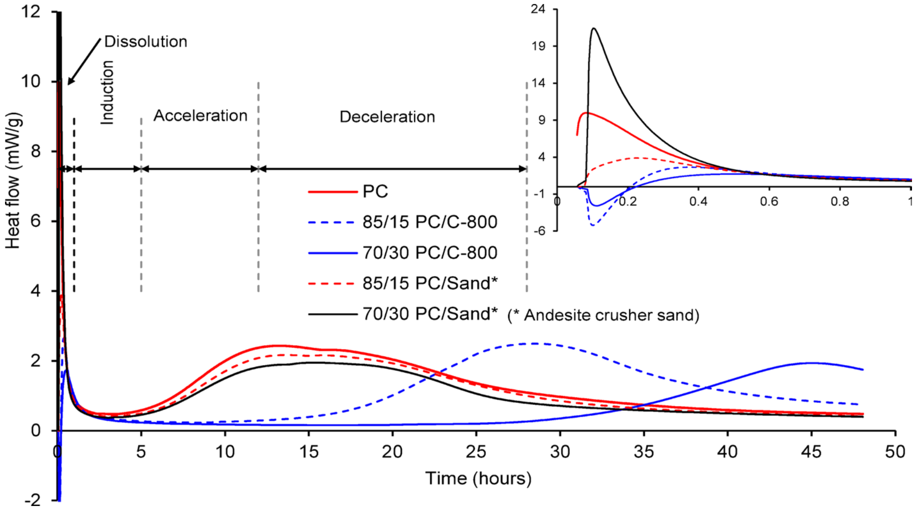

Fig. 4 Comparison of heat flow curves for PC, PC/C-800 and PC/Sand

differences in the heat flow curves can be attributed to the decrease in PC as a result of replacement with andesite crusher sand. This confirms the assumption that the andesite crusher sand is inert and did not contribute to heat evolution.

The heat flow curves in Figs. 3 and 4 show that the trends for the corn cob ash blends with PC are starkly different from those of plain PC and either PC/FA or PC/Sand blends. Contrary to the effect of the andesite crusher sand, it is clear that the replacement of PC with corn cob ash affected the heat evolution process. For the PC/C-700 corn cob ash blends (Fig. 3), there are unexpected intermediate heat peaks between the dissolution phase and the induction phase depicting the presence of chemical reaction(s). Such heat peaks were not observed in the PC/C-800 corn cob ash blends (Fig. 4). These observations can be attributed to the differences in the oxide compositions of the two corn cob ashes, specifically the high K_2O content, and the unburnt carbon content i.e. high loss on ignition [34] see Table 1. The dissolution of K_2O on contact with the mix water increases the pH of the solution which can induce further dissolution of C_3S and a likely reaction of C_3A beyond the first deceleration and prior to induction period. Huang and Yan [21] found that the addition of alkali is beneficial to the formation of AFt at very early ages especially for PC with high C_3A content. A likely interference between the dissociated Ca^{2+} and K^+ ions may have resulted in the retardation of the hydration reactions hence delaying progress to the induction phase. Odler and Wonnemann [30] have reported that the hydration of C_3A is accelerated in cement clinker with high K_2O although no effect was noted on C_3S hydration. It is important to note that the timing and value of the peak heats was inversely related to the PC replacement levels, with the peak in the blend with the lower PC replacement level (15%) occurring earlier and having a higher peak, and vice versa.

3.2.1 Dissolution phase

The peak of the heat flow in the dissolution phase was lower in the PC/FA and PC/CCA blends than in plain PC and PC/Sand specimens showing that both fly ash and corn cob ash influenced the rate of heat evolution. The lower heat flow rate in both the PC/FA and PC/CCA blends can be attributed to their dilution effect due to reduced plain PC content and the expected delayed early-age pozzolanic reactions [7]. Effectively, the heat evolution in the PC/FA and PC/CCA blends is mainly attributed to the exothermic PC hydration reactions especially due to the dissolution of C_3S (Bullard et al., 2011). It is important to note that the initial negative heat flows in this phase as depicted in Figs. 2, 3, 4 and 5 are related to the sensitivity of the isothermal equipment used in the experiments.

3.2.2 Induction phase

The results show that replacement of PC with corn cob ash extended the duration of this phase in comparison to that for fly ash, with a relatively longer induction period in the PC/C-800 blends. It is however important to observe that in the PC/C-800 blends, the degree to which the duration of the induction period was extended was directly related to the level of PC replacement with a higher PC replacement level resulting in a longer extension. The PC/C-700 blends had not clear trend in this regard. This showed that increasing CCA content has an effect on plain PC hydration and as such increasing content has no advantage on the system and subsequent properties with age. The influence of CCA on the induction phase is attributed to the low rate of heat evolution during the dissolution phase leading to slow dissolution of C_3S and slow growth of initial C-S-H formed [9]. This results in a low concentration of Ca^{2+} in solution while the absorption of the ions on CCA surface further delays the nucleation and growth of C-S-H [20].

3.2.3 Acceleration phase

The main heat peak that was observed in all the samples is a characteristic feature of the acceleration phase. Both the PC/FA and PC/Sand blends showed heat flow curves similar to that for plain PC albeit a relatively lower peak. This was expected due to the reduced PC content in the PC blends. For fly ash, the heat flow is further influenced by the content of the ash with the acceleration slope occurring slightly later at 30% than at 15% depicting a dilution effect of fly ash inclusion in the blend. In the PC/CCA blends, the evolution of this phase was delayed due to the prolonged induction phase as discussed previously. A general trend with respect to peak heat in the PC/CCA blends is that (i) replacement of PC with corn cob ash resulted in a lower rate of increase in heat flow in this phase, and (ii) the peak heat decreases with increase in PC replacement level.

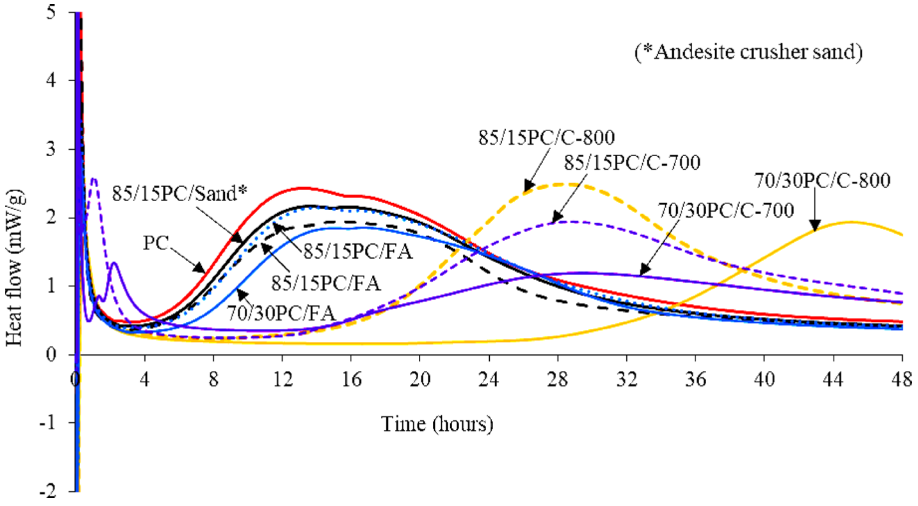

Fig. 5 Comparison of heat flow curves for PC, PC/FA, PC/C-700, PC/C-800 and PC/Sand

These trends further reinforce the assertion that the corn cob ashes used were not pozzolanic, and that the material has an inherently high heat capacity. The latter results in the delay of the acceleration phase. PC/C-700 blends have lower heat flow peaks than both plain PC and fly ash with the 85/15 PC/C-700 blend having a higher peak heat than the 70/30 PC/C-700 blend. Also, the deceleration slope for the 30% ash content can hardly be distinguished from the main heat peak showing that it has an influence on the mechanism controlling the phase while the rate of heat evolution following the induction phase was very low.

The evolution of the main heat peak in the acceleration phase has been attributed to the nucleation and growth of C-S-H, reaction of the aluminate phases and formation of the AFt and AFm phases [15]. These phenomena terminate the slow reaction period in each of the systems leading to increase in the rate of heat evolution beyond the induction phase. A consideration of the phenomena controlling this phase show that the corn cob ash has a more pronounced effect on the phenomena than fly ash. The differences can be traced to their chemical and mineralogical compositions which further influence their interaction with plain PC and affects the hydration reaction. The chemical and mineralogical aspects relate to, respectively, the relatively high K_2O of the corn cob ashes which influences the binding potential of the dissociated K^+ ions to C-S-H, and the finer and more reactive fly ash particles which enhance nucleation and growth of hydration products better than those for corn cob ash. The lower heat peak in C-700 compared to fly ash and sand can be attributed to a lower nucleation and growth rate of C-S-H and reaction of aluminates. The higher heat peak in C-800 compared to C-700 can be linked to its reduced unburnt carbon content (low LOI) with its particle providing more surface area for the nucleation and growth of C-S-H as well as enhancing the formation of the AFt and AFm phases. This effect becomes significant with an increase in the ash content.

3.3 Rate of heat rise and total heat

Figures 6, 7 and 8 show the total heat curves for the different binder systems used while Fig. 9 presents the total heat values measured after 48 h in the isothermal calorimeter test. These results show that (i) replacement of PC with corn cob ash had negative effect on the rate of heat rise, with the effect increasing with increase in PC replacement level,

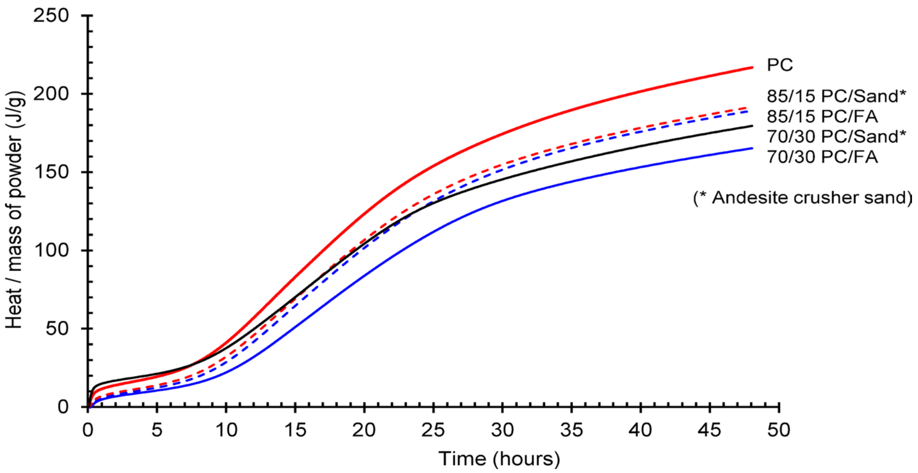

Fig. 6 Comparison of total heat curves for PC, PC/FA and PC/Sand

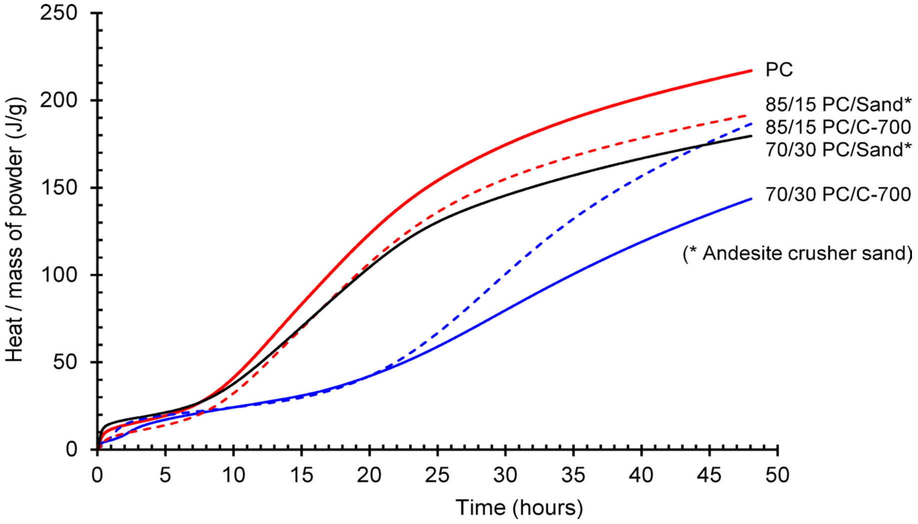

Fig. 7 Comparison of total heat curves for PC, PC/C-700 and PC/Sand

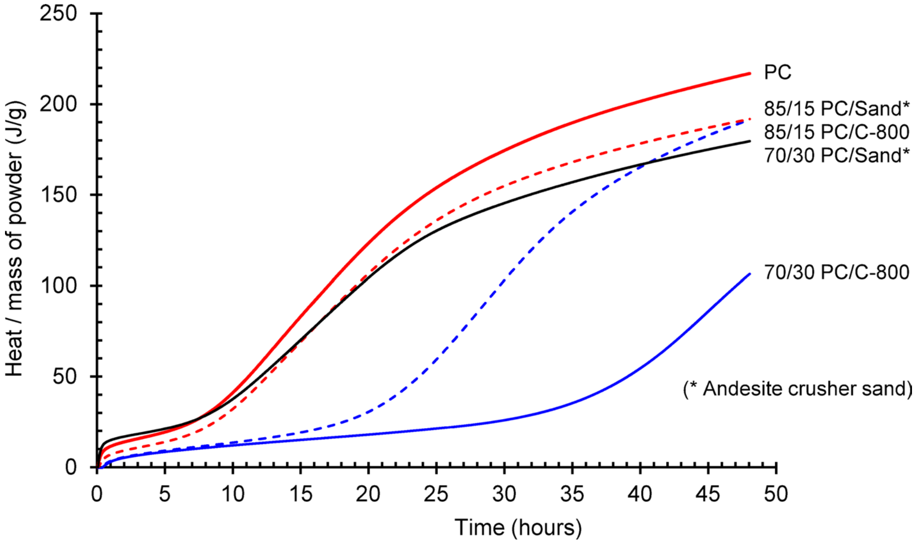

Fig. 8 Comparison of total heat curves for PC, PC/C-800 and PC/Sand

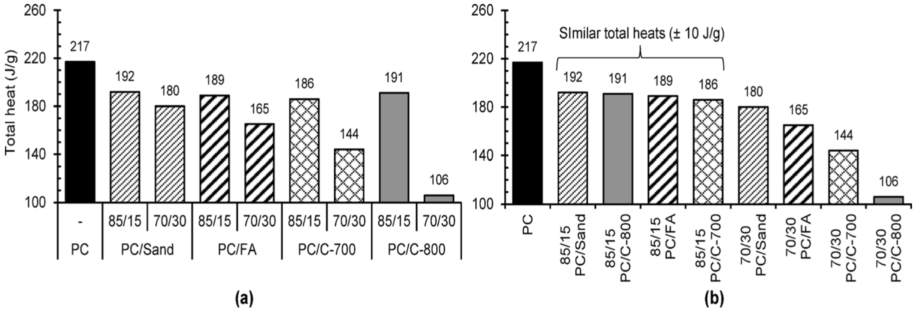

Fig. 9 Total heat values measured after 48 h

and (ii) replacement of PC with corn cob ash (C-700 and C-800) at 15% did not affect the total heat (see Fig. 9).

3.4 Strength development and strength activity index

Figure 10 presents the 28-, 56- and 90-day compressive strength results of the mortar specimens made using the different binders. The later-age strengths were measured to assess the effect of delayed pozzolanic, if any, on strength. To achieve this, it was necessary to quantify the percentage increase in strength with time. The increase in compressive strength from 28-day to 90-day age for PC, PC/FA, PC/C-700 and PC/C-800 were, respectively, 14%, 24%, 10% and 9%. The increases are minimal except for PC/FA. This trend was expected as fly ash is a known pozzolanic material [36]. More importantly, these results depict the non-pozzolanicity of the corn cob ashes. It is however noteworthy that corncob ash C-700 had a lower 90-day compressive strength than corn cob ash C-800, 36 MPa and 44 MPa respectively. This can be attributed to its high unburnt and carbon content in the corn cob ash C-700 (see Table 1) as evidenced by the high value of the LOI and high K_2O content. On the one hand, unburnt carbon is non-reactive and therefore does not contribute to strength [35]. On the other hand, the high K_2O content increases the potential of the silica binding to K^+ instead of Ca^{2+} leading to formation of a modified C-S-H and C-A-S-H structure with a weakly bonded matrix and hence low compressive strength [25, 26].

Figure 10 is a plot of the strength activity index (SAI) values of the mortar mixes. ASTM C 618 stipulates a minimum SAI of 75% for a material to be classified as pozzolanic. The results (see Figure 11) show that both fly ash and corn cob ash C-800 exceeded this value for all ages. As already mentioned, fly ash is a known pozzolanic material and the result was expected. In the case of the corn cob ash C-800, these results indicate that the material potentially exhibits relatively lower pozzolanic properties compared to fly ash. This can be attributed to the low amorphous content in the corn cob ash that can only sustain an increase in SAI up to the age of 56 days – see Table 1.

More importantly, the largely crystalline nature of the corn cob ashes C-700 and C-800 leads to the conclusion that the materials act more like filler materials than cementitious

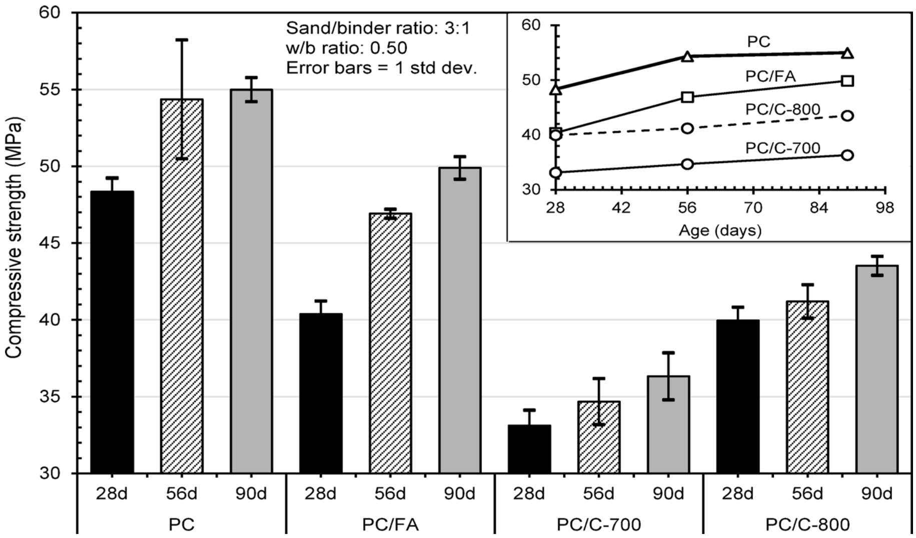

Fig. 10 Compressive strength results

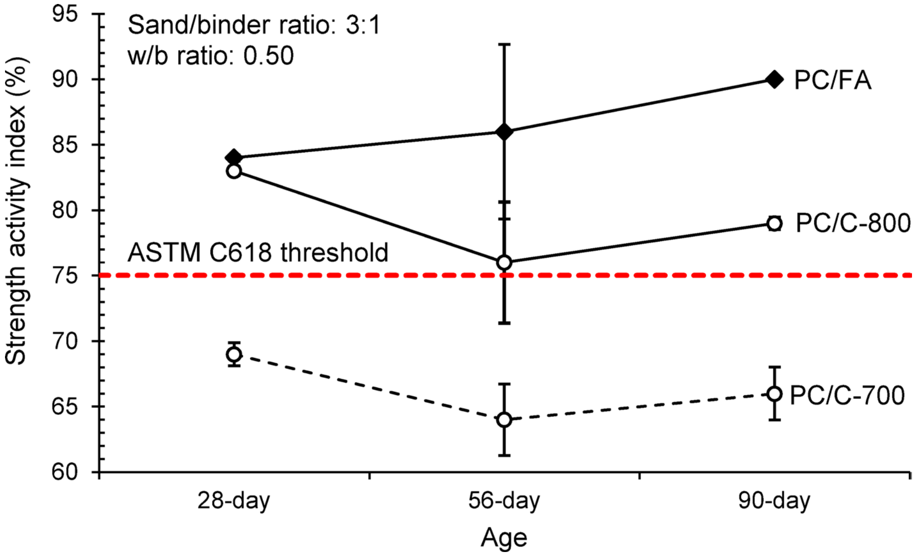

Fig. 11 Variation of strength activity index with age

Table 2 Bound water content of paste (R^3 Test)

Material	FA	C-800	C-700	Sand
Bound water (g/100 g)	6.16	3.44	2.89	1.73

(i.e. pozzolanic) ones. Consequently, it can be expected that the materials play a physical fine-filler effect in enhancing strength. It is therefore important to take this into account when interpreting the SAI values. Even though one of the corn cob ashes exceeded the ASTM C 618 threshold, it cannot be taken to expressly mean inherent pozzolanicity of the material if the material properties are considered [23]. Testing up to the age of 90 days can be considered to have mitigated against this limitation with respect to delayed pozzolanic reactions. However, it does not eliminate the likelihood of activity such as nucleation [31] on the surface of crystalline materials like the corn cob ashes. The SAI values should therefore be interpreted together with other tests especially when dealing with non-conventional cementitious materials. That the 75% SAI requirement is met by a material indicates its potential for use as a supplementary cementitious material but its usefulness will require further testing of its performance especially on strength and durability.

3.5 Bound water content

The bound water contents of pastes prepared with FA, Sand, C-700 and C-800 are presented in Table 2. The results depict the quantity of chemically bound water in the hydrates formed in the paste that is released when the sample is exposed to a temperature of 350 °C. The bound water values for C-700 and C-800 fall within the range of bound water defined by that for the sand (an inert material) and that for fly ash. Inasmuch as it is inexplicable why the sand sample had a non-zero bound water result, it is still important as a reference point. As mentioned earlier, fly ash is a known pozzolanic material and was expected to exhibit bound water in the aluminate and silicate compounds [3]. The higher bound water content in the corn cob ashes than in the sand is a clear indication that some degree of pozzolanic reaction leading to the formation of hydrates with bound water took place. This was however limited by the low amorphous content in the material.

4 Conclusions

The characteristics of corn cob ash and its influence on the hydration kinetics and strength activity index of ash-blended cementitious systems was studied. Two corn cob ashes were obtained mainly by the calcination of raw corn cobs at two temperatures vis-a-vis 700 °C and 800 °C. The results show that:

(a) the influence of corn cob ash on the hydration kinetics is majorly affected by its physical and chemical properties that are directly affected by the calcination process.

(b) A comparison of the amorphous content and R^3 test results indicate that the corn cob ashes used in the study exhibited minimal pozzolanic properties, if any. Despite this, the specimens made using the corn cob ashes met the strength activity index threshold value (ASTM C618) for classification as being pozzolanic, highlighting the limitation of the test method. Long-term performance testing is required to further understand the performance of corn cob ash in concrete and aid its proper classification;

(c) The high K_2O content of corn cob ash studied can be a major limitation to its use in cementitious system as this can potentially increase the risk of alkali-silica reaction in concrete.

(d) Corn cob ash influenced the hydration process of plain PC, prolonging its induction period and delaying the evolution of the main heat peak. This was mainly attributed to the high K_2O content that was also responsible for the lower strength in the corn cob ash-blended cements.

(e) Corn cob ash showed a similar total heat to fly ash but its effect on the induction phase and main heat peak of hydration depicts it as a material with different reaction mechanism from fly ash. This will require further testing to ascertain its actual contribution/effect on strength performance of concrete.

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Author contributions
O.A.: Conceptualisation, Experimentation, Writing.M.O.: Conceptualisation, Supervision, Visuals and Review.

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Data availability
The data for this study will be made available by the authors on reasonable request.

Declarations

Ethics approval and consent to participate
The ethical clearance as duly approved by the University of the Witwatersrand School of Civil and Environmental Engineering Ethics committee was obtained for this research. The research has the consent of authors to participation and publishing.

Consent for publication
The research has approval of all authors for publication.

Competing interests
The authors declare no competing interests.

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