

Influence of Superabsorbent Polymers (SAP) on Fresh and Early-age Properties of High-Performance Concrete

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ABSTRACT

Superabsorbent polymer (SAP) addition as an internal curing (IC) agent in high-performance concrete (HPC) has been adjudged to be effective in mitigating autogenous shrinkage. The influence of SAP created voids fresh properties and early strength development of the HPC as cement hydrates is however yet to be well understood. This paper hereby presents a report of an experimental study on SAP incorporation as an internal curing agent in a low water/binder (W/B) HPC. Four reference HPC mixtures (M_{1F}, M_{1S}, M₂ and M₃) designed for a 28-day minimum cube compressive strength of 70 N/mm² (MPa) were examined for the effect of SAP grain size, content and binder type on setting times and degree of hydration. The study also involved the determination of the pH-value of the simulated cement pore solution obtained from the binder combination types and its influence on SAP absorbency in concrete. It was observed that the addition of SAP resulted to increase in the setting times, while the degree of hydration of the HPC mixtures was found to increase as SAP content increases. The higher the SAP grain size, content and W/B for all mixtures, the higher the chemically bound water (w_n) at specific times and this increased as the hydration period increases.

Keywords: Superabsorbent polymers (SAP), SAP absorbency, setting times, chemically bound water, rate of hydration, early-age strength.

INTRODUCTION

The incorporation of superabsorbent polymers (SAP) in concrete is gaining acceptance as an internal curing (IC) agent especially in high-performance and ultra-high performance concrete. However, the effect of its utilisation on cement hydration and strength development in these types of concrete is yet to be fully understood. Amongst the issues of concern is the effect of SAP on the fresh properties of concrete such as workability, setting times and rate of hydration. Also, the influence of the cement pore solution (CPS) concentration on the rate of fluid absorption and

desorption by SAP is of interest. Absorption of pore fluid into the SAP is believed to be the result of competitive balance between expansive and shrinkage forces. High concentration of ions existing inside the SAP, leading to water flow into the SAP by osmosis and the increase in swelling due to water solvation of hydrophilic groups present along the polymer chain, are seen as the main factors responsible for rate of absorbency (Mechtcherine & Reinhardt, 2012). Mönnig (2009) reported that the calcium (Ca^{2+}) ions present in the pore solution of concrete could cause additional interlinking of the polymers and limit their swelling. Jensen & Hansen (2001) argued that the increase in the concentration of the Ca^{2+} ions outside the SAP results in decrease in osmotic pressure inside the gel and hence a reduced swelling of the SAP. This study therefore examines simulated CPS for different water/binder ratios (W/B) for an evaluation of the SAP absorbency.

RESEARCH SIGNIFICANCE

The work of Lothenbach and Winnefeld (2006) is one of the many studies on concentration of different ions in CPS as a function of hydration time of cement. The potassium (K^+), sodium (Na^+) and sulphate (SO_4^{2-}) ions are the highest concentration commonly found in a CPS. Lura & Lothenbach (2010) observed that high concentration develops immediately after mixing and remains roughly constant until the setting time. The ionic strength is noted to decrease at later ages as a result of precipitation. Lura & Lothenbach (2010) further posited that the ionic strength of CPS differs considerably among Portland cements depending on their alkali contents. Supplementary cementitious material (SCM) is argued to further influence the ionic strength (Lura & Lothenbach, 2010). Studies on SAP absorbency had been purely on synthetic pore solution with none in literature examining different simulated cement pore concentration and its effect on absorbency. Little is also known on the influence of SAP as IC-agent in low W/B HPC on its fresh properties and the rate of cement hydration. It is on this premise that this study investigates the influence of SAP as an IC-agent on the workability, settings times and degree of cement hydration in the low W/B high-performance concrete (HPC). Effects of SAP grain size and content were also studied on the aforementioned fresh and early age strength properties.

EXPERIMENTAL PROCEDURE

Materials

The materials used for this study include SAP, natural sand, crushed greywacke stone, cement, silica fume (SF), fly ash (FA), corex slag (CS), water and superplasticiser. The SAP is a thermoset polymer, specifically, the covalently cross-linked polymers of acrylic acid and acrylamide, neutralised by alkali hydroxide produced by SNF Floerger in France. Two grain sizes of SAP (< 300 μm [0.012 in.] with product label FLOSET CS 27 and < 600 μm [0.024 in.], labelled FLOSET CC 27) as specified by the manufacturer were used with the SAP contents varied (0%, 0.2%, 0.3%, and 0.4% by weight of binder (b_{wob})).

Cement CEM I 52.5 N supplied by PPC, South Africa conforming to BS EN 197-1-2000 and SANS 50197-1 served as the main binder. SF, by SiliconSmelters of the FerroAltantica group; FA from AshResources and CS supplied by PPC; all in powdered form were used as SCM for the various HPC mixtures as required by the mix design. The blends of the binders were categorised into three types as follows:

Binder Type 1 is the combination of CEM I 52.5 N and SF (7.5% b_{wob}) which is also referred to as binary cement and adopted for reference HPC mixtures M_2 (0.25 W/B) and M_3 (0.30 W/B). Binder Type 2 is composed of CEM I 52.5 N, SF (7.5% b_{wob}) and FA (17.5% b_{wob}) used for M_{1F} (0.2 W/B), while Binder Type 3 is made of CEM I 52.5 N, SF (7.5% b_{wob}) and CS (17.5% b_{wob}) used for M_{1S} (0.2 W/B). Binder Types 2 and 3 are referred to as ternary cements. The mix constituents for the reference HPC mixtures made with the respective binder types can be found in an earlier article (Olawuyi & Boshoff, 2017).

Natural sand with minimum particle size of 300 μm [0.012 inch] (i.e. all the particles smaller than 300 μm [0.012 inch] removed using the sieving method [sieve No. 50]), having fineness modulus, $\text{FM} = 2.79$, Coefficient of uniformity – $C_u = 2.43$, Coefficient of curvature, $C_c = 1.02$ and dust

content = 0.3% was used as fine aggregate. This conforms to medium sand classification according to Shetty (2004). 13 mm [0.52 in.] crushed Greywacke stone served as coarse aggregate in compliance with typical HPC mixes found in literature (Beushausen & Dehn, 2009; Neville, 2012). The crushed stone was washed and spread in the open air for surface drying before measuring the required quantity for the reference HPC mixtures. This was to reduce the dust content of the coarse aggregate in order to achieve low water demand for the HPC mixtures, especially the M_{1F} and M_{1S} with extremely low W/B.

Method

Simulated CPS were made for various W/C paste with a W/C of 5.2 representing a CPS from a typical 0.42 W/B paste or concrete, while simulated CPS were made for the 0.35 W/B (using W/C of 4.3); 0.3 W/B (W/C of 3.7); 0.25 W/B (W/C of 3.1); 0.2 W/B (W/C of 2.5) pastes/concrete. The above mentioned simulated CPS was adopted for determination of the SAP absorbency in the CPS containing purely PC and water using the tea bag test method (EDANA, 2002). The binary and ternary CPS were then made with the proportion of the SCMs incorporated for the binder combinations appropriately calculated and the pH-values determined.

The early age cement hydration and strength properties tests involved four reference HPC mixtures of different binder combination types as mentioned in Section 3.1 and W/B (M_{1F} & M_{1S} (0.2), M₂ (0.25) and M₃ (0.3)) for a minimum 28-day characteristic strength of 70 N/mm² [MPa] minimum (i.e. C55/67 – C100/115 HSC) designed using Aitcin (1998) method for HPC. Other HPC mixtures having varied SAP contents (0.2%; 0.3% and 0.4%) for the two SAP sizes (SP₁ – the smaller and SP₂) were then made for the respective reference HPC mixtures with extra water provided for SAP absorption on the basis of 25 g/g determined using the tea-bag test.

The concrete production process involved first adding the fine aggregate to the 50-litre capacity pan-mixer, followed by the binders which had first been thoroughly hand-mixed to ensure even dispersion of the SF and the other SCMs (FA or CS as appropriate) until a uniform colour was observed. After mixing for about 30 seconds, the dry SAP particles were added and all the fine contents mixed for another 30 seconds. The coarse aggregate were added and mixing continued for another 1 minute. Thereafter, water already mixed with superplasticiser (Chryso fluid Premia 310 – a PCE) was added. The mixing was allowed to continue for another 3 minutes as recommended in literature (Aitcin, 1998, Neville, 2012; Mehta & Monteiro, 2014).

Slump flow measurement was carried out using the flow table test (described in BS EN 12350 – 5:2009) as a measure of workability of the HPC mixtures, while both the room and concrete temperature were also measured using a digital pocket thermometer (Checktemp 1, Model No. H1-740024 by HANNA Instruments Incorporated). After ascertaining that the mixture met the required workability and cohesion for the specified design mix, specimen for various fresh and early age strength properties tests were prepared as explained in details in the following sub-section.

Setting time tests

The setting times (initial and final) of the HPC mixtures were determined using a penetration resistance method in accordance to ASTM C403 – 08. Using a standard 4.75 mm sieve [sieve No. 4], mortar samples were extracted from the fresh HPC mixtures and cast in two layers into 150 mm [6 in.] cube moulds to about 10 mm [0.4 in.] below the height edge. The specimens were kept in a climate control room set at a temperature of 21±2 °C [61.8 ± 2°F] temperature and 65±5% relative humidity. A penetrometer Model C213, by Matest S.P.A., USA was used to measure the resistance of the concrete to 25 mm [1 in.] depth penetration of respective needle heads beginning from the largest as specified by the code at regular 30 minutes intervals. The plot of penetration resistance (on ordinate axis) against time in minutes (abscissa axis) gives the initial (3.5 N/mm² [MPa] resistance) and final setting (27.6 N/mm² [MPa] resistance) times, respectively, using a direct fitting on a powers regression line.

Degree of hydration of HPC with SAP

An assessment of early age strength development and degree of hydration of HPC with SAP was conducted on sieved mortar samples of HPC mixtures obtained as explained in Section 3.2.1. The

study adopted the same approach as reported by Hasholt et al. (2010). The process is highlighted in the following stages.

- i. Mortar samples (50 mm [2 in.] cube) were cast and crushed after different curing ages (i.e. immediately after demoulding, 24 hrs, 48 hrs, 72 hrs and 7 days) to assess the strength development of the HPC with SAP.
- ii. The remains of the sample in (i) above was then milled properly using the mould for Aggregate Crushing Value (ACV) test and a 25 mm [1 in.] diameter bar as mortar and pestle. The milled sample was vacuum-dried for 1 hour to stop further hydration.
- iii. From the vacuum-dried sample, a known weight of about 50g from the particles passing the 300 μm standard sieve [sieve No. 50] was measured and oven dried for 24 hours at 105 $^{\circ}\text{C}$ [221 $^{\circ}\text{F}$] and weighed again (to determine the amount of evaporable water i.e. capillary water + gel water).
- iv. It was heated and kept at 950 $^{\circ}\text{C}$ [1742 $^{\circ}\text{F}$] for 1 hour and weighed (for determination of amount of chemically bound water). All calculations was then made based on ignited weight basis to give the following:

Loss on ignition (LOI) of the binders (CEM I 52.5 N, SF, FA and CS) and hydrated mortar pastes calculated by

$$\text{LOI (\%)} = 100 \times (\text{as received weight} - \text{ignited weight}) / \text{as received weight} \quad (1)$$

w_n (i.e. non-evaporable water) content of the hydrated mortar pastes were determined to evaluate the degree of hydration as provided for in literature (Lam et al., 2000; Neville, 2012). This is the difference in mass measurement of the crushed paste at 950 $^{\circ}\text{C}$ [1742 $^{\circ}\text{F}$] and 105 $^{\circ}\text{C}$ [221 $^{\circ}\text{F}$], to calculate the degree of hydration (α) on the basis that 1g [0.002205 lb.] of anhydrous cement produces 0.23g [0.000507 lb.] of w_n , hence the w_n is calculated by using the following formula

$$w_n \% = \frac{100 \times (\text{dried weight of paste} - \text{ignited weight of paste})}{(\text{Ignited weight of paste} - \text{loss on ignition of cement})} \quad (2)$$

The degree of hydration (α) is then:

$$\alpha = 100 \times \frac{w_n}{0.23} \quad (3)$$

The degree of hydration in the binary (M_2 and M_3) and ternary (M_{1F} and M_{1S}) cement pastes were however calculated with consideration for the LOI of the SCM and their proportion made to adjust for their $w_n\%$ as appropriate.

EXPERIMENTAL RESULTS AND DISCUSSION

SAP Absorption in CPS

Results of the pH-values for the various simulated CPS and summary of SAP absorption after 10 minutes in the CPS is presented in Table 1.

Table 1: pH-values of CPS and SAP absorption

| Solution | Water | (W/C*) | (W/C) | (W/C) | (W/C) | (W/C) | M_2 | M_{1F} | M_{1S} |
|--------------------------------------|--------|--------|-------|-------|-------|-------|-------|----------|----------|
| | | 5.2 | 4.3 | 3.7 | 3.1 | 2.5 | | | |
| pH-value | 7.43 | 12.87 | 12.85 | 12.81 | 12.62 | 12.59 | 12.89 | 12.47 | 12.41 |
| Temp $^{\circ}\text{C}$ | 23.10 | 18.63 | 18.26 | 18.50 | 21.30 | 19.40 | 18.70 | 19.17 | 18.20 |
| 10 mins absorption (SP_1) | 228.44 | 24.30 | 21.64 | 24.08 | 22.77 | 27.24 | - | - | - |
| 10 mins absorption (SP_2) | 258.22 | 33.93 | 24.45 | 27.85 | 23.61 | 24.09 | - | - | - |

*W/C on this table is the content of water to cement for the simulated pore solution extracted from cement pastes and concrete according to the standards for the teabag test. The W/C of 5.2 represent a CPS from a typical 0.42 W/C paste or concrete, while simulated pore were made for the 0.35 W/B (using W/C of 4.3); 0.3 W/B (W/C of 3.7); 0.25 W/B (W/C of 3.1) 0.2 W/B (W/C of 2.5) pastes/concrete respectively.

Details of SAP absorption for the entire test period of 180 minutes is presented in Olawuyi (2016 – Table A2). All the CPS gave pH-values ranges of 12.4 – 13.0, implying they are all alkaline in nature. This is typical for concrete especially those made with Type II cement (i.e. usually CEM I blended with SCMs especially the ternary cements with Al₂O₃ and Fe₂O₃ (alkaline) contents contribution from FA and CS) as pointed out in Kakade (2014).

The pH-values decrease slightly as the water content in the CPS increases, while the CPS from binary cements (CEM I 52.5 N and SF) has similar pH-values (12.8 to 12.9) as the CPS made from only CEM I 52.5 N simulated for concrete having W/B of 0.2 to 0.3. The CPS made from ternary cements (CEM I 52.5 N, SF and FA or CS) on the other hand has pH-values (12.47 (M_{IF}) and 12.41 (M_{IS})) which are slightly below 12.5 (the expected minimum value range for Type II cement). The values are however within the range for high alumina cement (Kakade, 2014). The pH test for distilled water gave a value of 7.43, which is within the level for a neutral solution, although this was conducted on a hot day (with a temperature of about 23 °C [23.4 °F]) as opposed to the remaining solutions (recorded a temperature of about 18 °C [64.4 °F]) as shown in Table 1.

SAP absorption in the CPS after 10 minutes durations were generally within the range of 22 g/g [22 lb/lb] to 27 g/g [27 lb/lb] (mostly around 24 g/g [24 lb/lb] for both SAP grain sizes with few inconsistencies) while the observed slight differences is of no particular pattern. The round up average of 25 g/g was taken as the SAP absorption capacity in CPS and adopted for the HPC mixtures in this study. SAP absorption in water on the other hand is taken as 230 g/g (SP₁) and 260 g/g (SP₂).

Fresh Properties of HPC with SAP

Tables 2 (for binary cements) and 3 (for ternary cements) present the result of fresh properties test on the HPC mixtures with SAP. It reveals that the total W/B increases as the SAP content increases while the slump flow values on the other hand remain in the same range for all HPC mixtures (530 to 570 mm [21.2 to 22.8 in.] – M₂; 450 to 500 mm [18 to 20 in.] – M₃; 550 mm to 600 mm [22 to 24 in.] – M_{IF} and 450 to 500 mm [18 – 20 in.] – M_{IS}). The HPC mixtures containing FA (i.e. M_{IF}) is more flow-able than the one containing CS (M_{IS}) even though they are of same W/B. This is an indication that the FA, known to be of good and distinct inter-particle spaces gave better performance in enhancing improved workability of the low W/B HPC mixture. M₂ (0.25 W/B) is also more flow-able than M₃ (0.30 W/B) due to its higher superplasticiser content.

Table 2: Mix constituents and fresh properties of HPC mixtures from binary cements

| Constituents (kg/m ³) | M ₂ | | | | | | | M ₃ | | | | | | |
|--------------------------------------|----------------|-----------------|------|------|-----------------|------|------|----------------|-----------------|------|------|-----------------|------|------|
| | Ref | SP ₁ | | | SP ₂ | | | Ref | SP ₁ | | | SP ₂ | | |
| SAP contents% | 0.0 | 0.2 | 0.3 | 0.4 | 0.2 | 0.3 | 0.4 | 0.0 | 0.2 | 0.3 | 0.4 | 0.2 | 0.3 | 0.4 |
| Water | 134 | 134 | 134 | 134 | 134 | 134 | 134 | 156 | 156 | 156 | 156 | 156 | 156 | 156 |
| Cement | 540 | 540 | 540 | 540 | 540 | 540 | 540 | 500 | 500 | 500 | 500 | 500 | 500 | 500 |
| SF | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 | 40 |
| FA | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| CS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| C. Aggregate | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 |
| F. Aggregate | 710 | 710 | 710 | 710 | 710 | 710 | 710 | 700 | 700 | 700 | 700 | 700 | 700 | 700 |
| SAP | 0.00 | 1.16 | 1.74 | 2.32 | 1.16 | 1.74 | 2.32 | 0.00 | 1.08 | 1.62 | 2.16 | 1.08 | 1.62 | 2.16 |
| S/plasticizer | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 16.0 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 | 5.4 |
| Additional Water | 0.0 | 29.0 | 43.5 | 58.0 | 29.0 | 43.5 | 58.0 | 0.0 | 27.0 | 40.5 | 54.0 | 27.0 | 40.5 | 54.0 |
| Total W/B | 0.25 | 0.30 | 0.33 | 0.35 | 0.30 | 0.33 | 0.35 | 0.30 | 0.35 | 0.37 | 0.40 | 0.35 | 0.37 | 0.40 |
| Slump Flow | 550 | 530 | 580 | 550 | 550 | 580 | 570 | 500 | 500 | 500 | 450 | 460 | 450 | 450 |
| Room Temp. °C | 19.0 | 17.0 | 17.0 | 16.0 | 14.0 | 16.5 | 16.1 | 18.0 | 19.5 | 19.5 | 19.5 | 18.0 | 16.0 | 16.0 |
| Conc. Temp. °C | 26.0 | 24.0 | 23.0 | 22.0 | 21.0 | 21.8 | 20.3 | 22.0 | 23.6 | 23.5 | 23.5 | 20.0 | 18.0 | 18.0 |
| Design Density* | 2490 | 2520 | 2535 | 2550 | 2520 | 2535 | 2550 | 2451 | 2479 | 2494 | 2508 | 2479 | 2494 | 2508 |
| Demoulded Density | 2486 | 2457 | 2431 | 2407 | 2469 | 2429 | 2409 | 2413 | 2399 | 2344 | 2357 | 2382 | 2405 | 2394 |

*Note that the “design density” (dd) in Table 2 and 3 for HPC with SAP was arrived at by the addition of the weight of SAP and extra water added for SAP absorption to the initial calculated weight in kg/m³ for the reference mixture, hence the increase. The “demoulded density” (dmd) was determined by dividing the direct weight of the demoulded concrete with the measured volume of individual concrete cube. The density value at a specific curing age was the average of three specimens for that age divided by the average of the demoulded densities for all the twelve specimens of an HPC mixture.

Table 3: Mix constituent and fresh properties of HPC mixtures from ternary cements

| Constituents (kg/m ³) | M _{1F} | | | | | | | M _{1S} | | | | | | |
|--------------------------------------|-----------------|-----------------|------|------|-----------------|------|------|-----------------|-----------------|------|------|-----------------|------|------|
| | Ref | SP ₁ | | | SP ₂ | | | Ref | SP ₁ | | | SP ₂ | | |
| SAP Contents% | 0 | 0.2 | 0.3 | 0.4 | 0.2 | 0.3 | 0.4 | 0 | 0.2 | 0.3 | 0.4 | 0.2 | 0.3 | 0.4 |
| Water | 125 | 125 | 125 | 125 | 125 | 125 | 125 | 125 | 125 | 125 | 125 | 125 | 125 | 125 |
| Cement | 530 | 530 | 530 | 530 | 530 | 530 | 530 | 530 | 530 | 530 | 530 | 530 | 530 | 530 |
| SF | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 | 52.5 |
| FA | 122 | 122 | 122 | 122 | 122 | 122 | 122 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| CS | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 122 | 122 | 122 | 122 | 122 | 122 | 122 |
| C. Aggregate | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 | 1050 |
| F. Aggregate | 590 | 590 | 590 | 590 | 590 | 590 | 590 | 590 | 590 | 590 | 590 | 590 | 590 | 590 |
| SAP | 0.00 | 1.41 | 2.12 | 2.82 | 1.41 | 2.12 | 2.82 | 0.00 | 1.41 | 2.12 | 2.82 | 1.41 | 2.12 | 2.82 |
| S/plasticizer | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 | 21.0 |
| Additional Water | 0.00 | 35.3 | 52.9 | 70.5 | 35.3 | 52.9 | 70.5 | 0.00 | 35.3 | 52.9 | 70.5 | 35.3 | 52.9 | 70.5 |
| Total w/b | 0.20 | 0.25 | 0.28 | 0.30 | 0.25 | 0.28 | 0.30 | 0.20 | 0.25 | 0.28 | 0.30 | 0.25 | 0.28 | 0.30 |
| Slump Flow | 570 | 550 | 550 | 560 | 550 | 600 | 550 | 450 | 450 | 500 | 500 | 500 | 500 | 550 |
| Room Temp. °C | 16.0 | 16.0 | 16.0 | 16.5 | 16.5 | 16.0 | 16.0 | 11.5 | 11.0 | 15.0 | 14.0 | 15.0 | 14.0 | 15.0 |
| Conc. Temp. °C | 23.0 | 22.0 | 21.0 | 22.0 | 23.0 | 23.0 | 23.5 | 20.0 | 18.5 | 20.0 | 18.0 | 20.0 | 18.0 | 19.5 |
| Design Density * | 2491 | 2528 | 2546 | 2564 | 2528 | 2546 | 2564 | 2503 | 2540 | 2558 | 2576 | 2540 | 2558 | 2576 |
| Demoulded Density | 2477 | 2417 | 2379 | 2394 | 2466 | 2402 | 2406 | 2498 | 2438 | 2444 | 2412 | 2450 | 2431 | 2412 |

All the HPC mixtures irrespective of mix composition or SAP contents had workability range (slump flow values of 450 – 600 mm [18 – 24 in.]) conforming to the provisions of literature (Aıtcın, 1998; ACI 363.2R - 1998; Beushausen & Dehn, 2009; Mehta & Monteiro, 2014; Neville, 2012). SAP addition and extra water provided for SAP absorption did not result in higher slump flow values. The mixtures were all of similar consistency even with SAP added and no segregation was observed. The difference between the room temperature and concrete temperature, which is a measure of the heat generated in concrete mixing process decreased gradually as the SAP content increased with reference HPC mixes having the highest temperature difference values.

Concrete made with binders containing SF are noted for high evolving heat of hydration with water reducers (lignosulfate based) often introduced as set retarders by reducing the evolved heat (Silica Fume Association, 2005). It can therefore be argued that the water-filled swollen SAP within the HPC during the vigorous mixing process possibly released some of the water absorbed, or serves as means of reducing the temperature rise through conduction, from the agitated solid constituents into the absorbed water within the SAP particles. This lowers the internal concrete temperature.

Setting Times of HPC with SAP

Figure 1 shows a plot of the penetration resistance (in MPa) against the elapsed time (in minutes on a logarithmic scale) for M₂ - HPC mixture fitted on a power regression line giving the setting times with the expression:

$$Y = (2E - 21)X^{8.8671} ; \text{ having a strong correlation } (R^2 = 0.9851)$$

Y in the expression represents the penetration resistance (PR); X represents the elapsed time and the regression constants c (2E – 21) and d (8.8671) are in similarity to the code’s (ASTM 403 – 08)

provisions. Plots for other individual mixtures were made in the study with similar expressions obtained as presented in Appendix A4 of Olawuyi (2016).

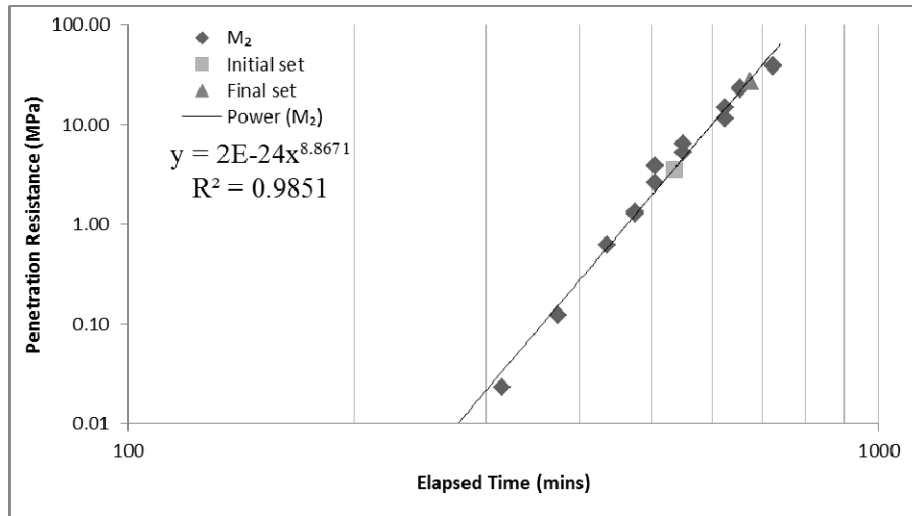


Figure 1: Setting times (initial and final) plot of M₂-HPC mixture

Result of setting times for the various M₂-HPC mixtures (with or without SAP) is shown in Figure 2. The results show that for these binary cement HPC mixtures, the setting time increases as the SAP content increased up to 0.3% b_{wob}, implying SAP addition generally resulted in set retardation.

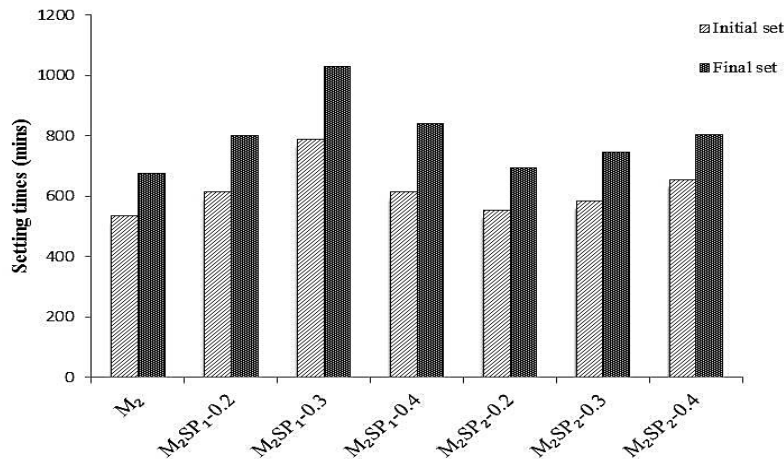


Figure 2: Initial and Final setting times for M₂-HPC mixtures made from binary cements

Figure 3 for M_{1S} – HPC mixtures (from ternary cements) show the same trend as in Figure 2 (M₂ – HPC, from binary cements). In both cases, SP₁ addition resulted in a steady increase in both initial and final setting time of the concrete. SP₂ addition on the other hand led to slower rate of increase in the setting times (initial and final).

Figure 4 shows all the HPC mixtures (M_{1F}, M_{1S}, M₂ and M₃) and influence of SP₁ contents on their initial and final setting times. In general, SP₁ addition led to longer setting times in all the HPC mixtures.

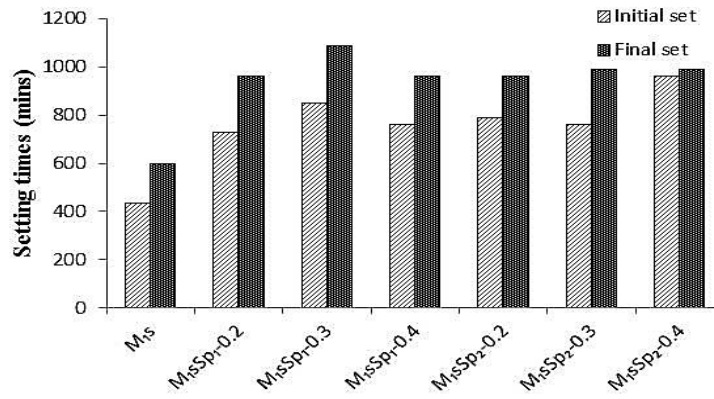


Figure 3: Initial and Final setting times of M_{1S} - HPC mixtures made from ternary cements

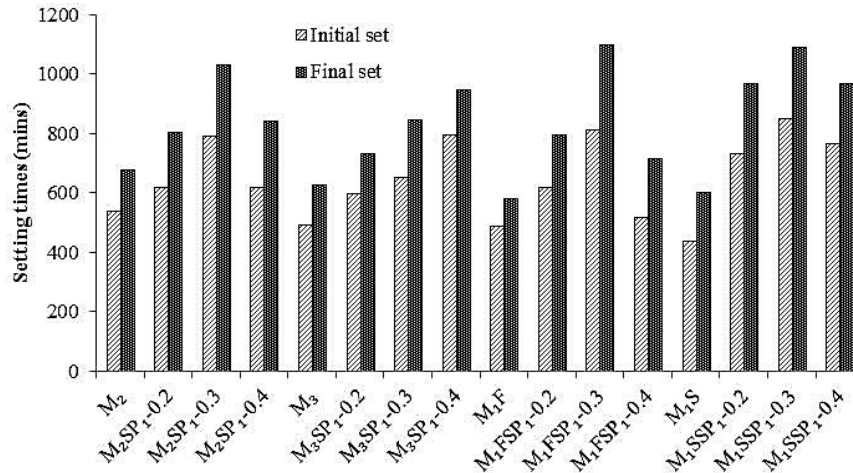


Figure 4: Initial and Final setting times of HPC mixtures with SP₁

Early Age Cement Hydration in HPC with SAP

Result of the degree of hydration is presented in Figure 5 (for binary cements, M₂ – HPC) and Figure 6 (ternary cements, M_{1S} – HPC). Summary of SAP influence on degree of hydration for all HPC mixtures studied is presented in Table 4. M_{1F} and M₃ mixtures were only examined for SP₁, while M₂ and M_{1S} were studied for both SP₁ and SP₂ to investigate influence of SAP grain sizes on rate of hydration when different binder combination types are used. The degree of hydration generally increased as the SAP content increases for all curing ages studied with an indication that SP₂ resulted in higher degree of hydration than SP₁ with few inconsistencies. Similarly, the higher the W/B, the higher the early-age hydration (M₃ – HPCs with the highest water content – 0.3 W/B recorded the highest degree of hydration). The relative rates of hydration called RH₇ factor (on basis of 7th day degree of hydration for reference mixtures) were highest for M_{1F} (the ternary cement HPC of 0.2 W/B containing FA). Influence of the SAP grain sizes in both binder combination types (binary – M₂ or ternary – M_{1S} cements) indicate that SP₂ resulted in higher hydration rate than SP₁ especially at 3 and 7 days curing ages (Figures 5 and 6).

The ternary cements HPC mixtures (M_{1S}), though with lower W/B, reflected a higher degree of hydration at the initial 24 hrs (values for the reference mixes are M_{1S} = 31.3% and M₂ = 25.0%); this however progressed at a slower rate than seen in the binary cements HPC mixtures (M_{1S} at 7-day = 39.2% while M₂ = 53.9%). This trend is maintained as SAP addition increased in the HPC mixtures. The degree of hydration between day 3 and 7 is however highest in the binary cement HPC mixtures (M₂ and M₃), with the mixture having the higher W/B (0.3) – M₃ – HPC displaying highest degree of hydration at these ages up to 7 days. The value by the 7-day was noted to be already above 60% for the specimen with highest SP₁ content (M₃SP₁-0.4).

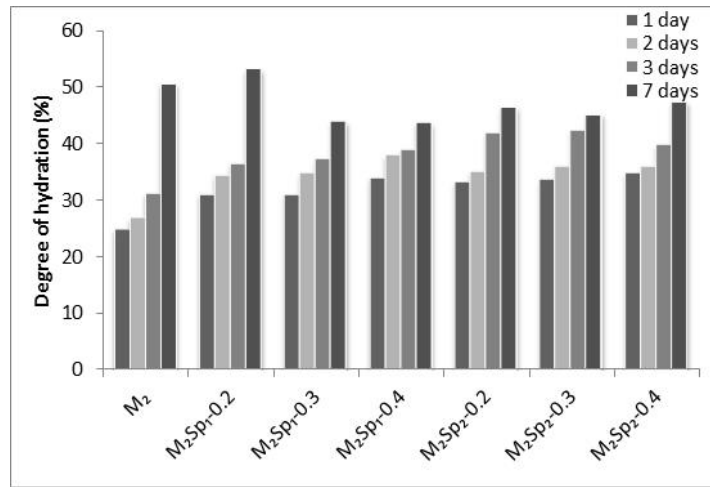


Figure 5: Degree of hydration of M₂-HPC (binary cements) with SAP

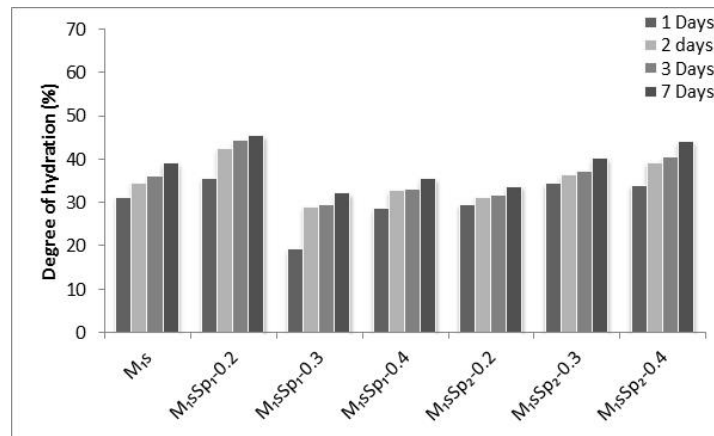


Figure 6: Degree of hydration of M_{1S}-HPC (ternary cements) with SAP

Table 4: Influence of SAP and binder type on degree of hydration of HPC

| Specimen | Degree of Hydration (%) | | | | RH ₇ Factor | | | |
|--------------------------------------|-------------------------|--------|--------|--------|------------------------|------|------|------|
| | 1 day | 2 days | 3 days | 7 days | 1 | 2 | 3 | 7 |
| M ₂ | 25.0 | 26.3 | 30.2 | 53.9 | 0.46 | 0.49 | 0.56 | 1.00 |
| M ₂ SP ₁ -0.2 | 31.2 | 32.9 | 34.4 | 54.0 | 0.58 | 0.61 | 0.64 | 1.00 |
| M ₂ SP ₁ -0.3 | 31.1 | 39.9 | 57.9 | 62.6 | 0.58 | 0.74 | 1.08 | 1.16 |
| M ₂ SP ₁ -0.4 | 34.2 | 38.1 | 63.2 | 65.5 | 0.63 | 0.71 | 1.17 | 1.21 |
| M ₂ SP ₂ -0.2 | 33.4 | 35.3 | 42.0 | 42.7 | 0.62 | 0.65 | 0.78 | 0.79 |
| M ₂ SP ₂ -0.3 | 33.4 | 36.2 | 42.5 | 48.8 | 0.62 | 0.67 | 0.79 | 0.91 |
| M ₂ SP ₂ -0.4 | 31.1 | 32.9 | 40.0 | 47.6 | 0.58 | 0.61 | 0.74 | 0.88 |
| M _{1S} | 31.3 | 34.6 | 36.2 | 39.2 | 0.80 | 0.88 | 0.93 | 1.00 |
| M _{1S} SP ₁ -0.2 | 35.7 | 42.6 | 44.4 | 45.5 | 0.91 | 1.09 | 1.13 | 1.16 |
| M _{1S} SP ₁ -0.3 | 19.3 | 29.2 | 29.7 | 32.3 | 0.49 | 0.74 | 0.76 | 0.82 |
| M _{1S} SP ₁ -0.4 | 28.8 | 33.0 | 33.2 | 35.7 | 0.73 | 0.84 | 0.85 | 0.91 |
| M _{1S} SP ₂ -0.2 | 29.7 | 31.2 | 31.7 | 33.9 | 0.76 | 0.80 | 0.81 | 0.87 |
| M _{1S} SP ₂ -0.3 | 34.5 | 36.4 | 37.5 | 40.4 | 0.88 | 0.93 | 0.96 | 1.03 |
| M _{1S} SP ₂ -0.4 | 34.1 | 39.3 | 40.7 | 44.2 | 0.87 | 1.00 | 1.04 | 1.13 |
| M _{1F} | 36.3 | 39.4 | 41.1 | 45.9 | 0.79 | 0.86 | 0.90 | 1.00 |
| M _{1F} SP ₁ -0.2 | 39.9 | 45.2 | 46.9 | 48.6 | 0.87 | 0.98 | 1.02 | 1.06 |
| M _{1F} SP ₁ -0.3 | 37.6 | 43.1 | 50.2 | 55.6 | 0.82 | 0.94 | 1.09 | 1.21 |
| M _{1F} SP ₁ -0.4 | 45.1 | 50.0 | 53.7 | 59.5 | 0.98 | 1.09 | 1.17 | 1.30 |
| M ₃ | 43.8 | 47.9 | 50.6 | 57.1 | 0.77 | 0.84 | 0.89 | 1.00 |
| M ₃ SP ₁ -0.2 | 47.6 | 50.6 | 52.0 | 58.6 | 0.83 | 0.89 | 0.91 | 1.03 |
| M ₃ SP ₁ -0.3 | 52.6 | 55.1 | 55.1 | 62.0 | 0.92 | 0.97 | 0.97 | 1.09 |
| M ₃ SP ₁ -0.4 | 53.9 | 56.6 | 57.8 | 65.1 | 0.94 | 0.99 | 1.01 | 1.14 |

Examining the binary cements HPCs (M_2 and M_3) reveals that the mixtures with higher W/B (M_3 -HPC, 0.3 W/B) exhibited higher degree of hydration at the initial 24 hrs but further hydration progressed at a decreasing rate as the SAP contents and curing age increased.

The RH₇ factor for the HPC mixtures containing SAP shows clearly that hydration increased as the SAP contents and W/B increases for all concrete at the respective ages of curing.

Two specimens ($M_{1S}SP_1-0.3$ and $M_{1S}SP_1-0.4$) did not conform to the observed trend of the experimental work in this aspect as the values obtained (green highlights on Table 4) is in variance. 0.2% b_{wob} for SP₁ content was however noted to give similar or even higher values as reference mixes in all cases and at all ages. The mixing water provided in the mix proportioning as a function of W/B can be considered as a major influence on hydration in general for these low W/B concretes at the early ages, as all mixtures studied had the same SF content. FA and CS addition in M_{1F} and M_{1S} retard the hydration process for the first two days; their inclusion however also improved workability and slump retention capacity for the extreme low W/B concretes.

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Inferences made from the experimental work reported here can be summarised as follows:

- i. All the simulated CPS studied gave pH-values ranges of 12.4 – 13.0, implying they are all of high alkaline nature as expected of concrete especially those made of Type II cement.
- ii. There was slight decrease in the pH-values as the water content of the CPS increases, while binder combination type and W/B also influence the concentration level observed in the CPS. Binary cements CPS were noted to give pH-values (12.8 to 12.9) similar to the CPS made from only CEM I 52.5 N and water simulated for concrete of 0.2 to 0.3 W/B. Ternary cements CPS had pH-values (M_{1F} – 12.47 and M_{1S} – 12.41) slightly below 12.5 (minimum expected for concrete made from Type II cement).
- iii. The CPS concentration had no significance influence on SAP absorption capacity as observed within the limit of W/C (5.2 to 10.4) and the binary and ternary cements (M_2 , M_{1F} and M_{1S}) concentrations as tested in this study.
- iv. SAP addition with extra water provided for its absorption had no direct influence on the consistency of the HPC mixtures examined. All the HPC mixtures irrespective of SAP contents and mix composition had slump flow values conforming to the reports in literature (Aïtcin, 1998; ACI 363.2R -1998; Beushausen & Dehn, 2009; Mehta & Monteiro, 2014; Neville, 2012).
- v. The temperature difference between room temperature and concrete temperature decreased gradually as the SAP content increased with reference mixes having the highest temperature difference values.
- vi. SAP addition in general resulted in longer setting times (both the initial and final) in all HPC mixtures. Setting time was observed to increase as SAP content increased up to a limit of 0.3%, hence SAP incorporation as IC-agent result in some level of set retardation. This is in agreement with the observation of Klemm (2009) that SAP addition led to longer dormant period.
- vii. The degree of hydration of the HPC mixtures increases as the SAP content increases with an indication that SP₂ resulted in higher degree of hydration than SP₁ in both binder combination types (binary – M_2 or ternary – M_{1S} cements). This is because the larger SP₂ grains resulted in bigger swollen SAP and hence higher water desorption at the early age for cement hydration. This finding agrees well with the postulation made by Mönnig (2009).
- viii. The higher the SAP content and W/B for all mixtures, the higher the chemically bounded water (w_{it}) at specific times and this increased as the hydration period increased.

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