Effect of Superabsorbent Polymer on the Hydration Properties of High-Performance Concrete

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Abstract—The physico-chemical and durability properties of the concrete depend on how efficiently the curing process occurs. Cement particles undergo a series of chemical reactions with water molecules to form several cement hydration products during curing. However, the low water to cement ratio in concretes, such as high-performance concrete (HPC) and ultra-HPC with supplementary cementitious materials, lack enough water molecules for the curing process to complete, resulting in autogenous shrinkage and hence early age micro cracking. Mitigation of shrinkage is a mandatory requirement in sustainable construction projects, which can be achieved through proper curing of HPC. This paper reports the effects of superabsorbent polymer (SAP) as internal curing material on the properties of hardened HPC monitored by N2adsorption, X-ray diffraction (XRD), and FT-IR spectroscopy after 28 days of curing in water and air. The N2 adsorption analysis showed an increase in total porosity of the specimens with SAP due to the formation of more macro pores. Higher amounts of Ca(OH)2 were detected in samples with SAP by the X-ray diffraction analysis indicating the formation of more cement hydration in those specimens.

Keywords—Internal curing, Superabsorbent polymer (SAP), High-performance concrete (HPC), N₂-Adsorption, X-ray diffraction, FT-IR

I. INTRODUCTION

During curing process cement particles undergo a series of chemical reactions with water to form several cement hydration products, which ultimately determine the final physico-chemical properties of hardened concrete [1]. Curing keeps the concrete saturated and prevents water loss by promoting the hydration process. However, the low water to cement ratio in special purpose concretes, such as high-performance concrete (HPC) and ultra-HPC with supplementary cementitious materials like metakaolin (MK) and silica fume (SF), lack enough water for the hydration process to complete and thereby resulting in autogenous shrinkage and early age micro cracking. The world wide acceptance and increasing applications of these special concretes attracted the use of internal curing material (ICM) to mitigate autogenous and drying shrinkage and improve concrete quality by promoting effective hydration. Not only special concretes, conventional concrete with low water-cement ratio require internal curing materials to provide effective concrete curing to avoid selfdesiccation and reduce autogenous shrinkage in the early ages, especially in those countries experiencing high ambient temperature and low relative humidity [2–4].

Superabsorbent polymers (SAPs) are important class of internal curing compounds used in cementitious materials. These highly cross-linked polymers form hydrogels by absorbing water up to 500 times their weight in an aqueous medium due to osmotic pressure [5]. Extreme care must be taken while using these materials in concrete as the osmotic pressure and hence the swelling capacity depends on the fluid composition of the mixture and chemical structure of the SAP. These hydrogels regularly release water in to the cementitious matrix regularly during cement hydration to maintain the relative humidity [5]. The water releasing effects of SAPs reduce the microporosity at the later ages by filling the pores with hydration products and reducing the autogenous shrinkage to minimize the initial micro-cracks in the cement matrix [6, 7]. However, the empty macro pores created by the shrinkage of SAPs can cause a negative effect on the mechanical properties [5].

Additional water was added to compensate for the loss of workability in concrete mixtures with SAP due to the uptake of mixing water by the SAP molecules [8-10] when compared with the reference mixture. The use of SAPs in concrete mixtures promotes autogenous healing [11, 12] along with increasing the freeze/thaw resistance [13, 14] and self-sealing [15–17] properties. SAPs can also influence the rheological properties of the fresh materials in the early ages of concrete mixing [18-20]. However, limited studies are conducted on the influence of SAP on the microstructural development of HPC [4, 5, 21-24]. This paper reports the effects of superabsorbent polymer (SAP) as an internal curing material on the development of hydration products and pore structure, monitored by N₂-adsorption, X-ray diffraction (XRD), and FT-IR spectroscopy after 28 days of curing in water and air.

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II. MATERIALS

Materials required for the preparation of high performance concrete, including ordinary Portland cement (Type-I, conforming to ASTM C150), washed sand. normal coarse aggregates (NCA). and polycarboxylate based superplasticizer (SP) were collected from the local market. A commercially available superabsorbent polymer (SAP) was used as internal curing material (ICM) for the present investigations. SAP samples were vacuum dried in a desiccator with silica gel prior to the mixing with concrete composite. The absorption of SAP was determined using the teabag test method according to RILEM TC 260 RSC [25], and the amount of the required SAP for the concrete mix was selected based on its absorption capacity. The bulk density of SAP is 0.7 g/ml, and the specific gravity is 2.7-3.1.

A. Experimental Methods

High performance concrete mix was designed for a strength of 50 MPa. The influence of SAP on the concrete properties were evaluated by preparing two concrete mixes with a w/c ratio of 0.35. This included the control mix (Mix 1-C35, 0.35 w/c ratio) and the mix with SAP (Mix 2-C35SAP-mix with SAP at 0.35 w/c). These samples were subjected to water and air curing for 28 days. Samples were collected from the concrete specimens after flexural strength test to evaluate the effect of internal curing material on the microstructural properties of concrete specimen. These samples were kept in acetone for one week by changing the acetone in every alternative day for arresting the hydration effectively. Samples were vacuum dried completely prior to the analysis. Nitrogen adsorption analysis was performed on chipped solid pieces of approximately 0.2-0.4 g. The experiments were performed with gas adsorption analyzer. The adsorption and desorption isotherms, surface area, and cumulative intruded volume were calculated using the data from the nitrogen adsorption experiment. The powdered samples were used for XRD and FT-IR analysis. The XRD analysis was performed with a Bruker D8 Advance powder diffractometer. In this apparatus, the Cu K α ($\lambda = 1.5418$ Å) was generated in a Cu tube at 40 kV and 40 mA. The tests were performed over Bragg angle (2 θ) range 5-70 ° with a scan speed of 1 s per step on the sample. FT-IR transmission spectra were recorded by Shimadzu-IR Tracer-100 spectrometer by the Attenuated Total Reflection (ATR) technique in the scan range of 400-4000 cm⁻¹.

The material safety data sheet provided by the suppliers showed that the ICM contains ground granulated blast furnace slag (GGBS), amorphous silica, crystalline silica, calcium salts, and partial sodium salt of cross-linked polypromancic acid. The FT-IR analysis (Fig. 1) of SAP showed a strong carbonyl stretching frequency at 1743 cm⁻¹ due to the salt formation from the parent acid derivatives along with a weak acyl (C-O) stretching frequency at 1159 cm⁻¹. The asymmetric and symmetric stretching frequencies of -CH₂ were observed

at 2924 cm⁻¹ and 2854 cm⁻¹ respectively as strong bands. Characteristic Si-O stretching frequencies were also noticed at 1159, 1093, and 1026 cm⁻¹. The XRD spectrum of the SAP showed a broad peak, characteristic of the amorphous nature of the material between 13–25 °2 θ as shown in Fig. 2.







III. RESULTS AND DISCUSSIONS

A. XRD Analysis

Oualitative X-ray diffraction analysis of concrete samples (C35 and C35SAP) after 28 days of curing in water and air is given in Fig. 3. The diffractogram showed the presence of quartz (SiO₂) from the aggregates, portlandite (Ca(OH)₂), calcite (Ca(CO₃)), a broad hump of C-S-H between 26 and 30 degrees two theta along with other crystalline CSH peaks, dolomite $(CaMg(CO_3)_2)$, and negligible amount of ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂ 26H₂O). The presence of C3S and C2S were also noticed in significant amounts [26]. No new phases were identified in the sample with SAP compared to the control sample. Only, the amount of these phases varied depending on the curing period and conditions.



Figure 3. X-ray diffraction analysis of Mix-1 and Mix-2 concrete samples after 28 days of curing in water and air.

As expected, after 28 days of curing, samples cured under water contain more calcium hydroxide (CH) and calcium silicate hydrates (C-S-H) compared to the air cured samples. Even though there is not much difference in the amounts of CH for water cured samples, the sample with SAP (C35SAP-A) has more CH content than the sample without SAP (C35-A) under air curing. This clearly indicates that the water releasing effect of SAP molecules promotes cement hydration process [22, 27]. The highest amount of calcium carbonate was detected in the control sample cured under air condition. The air cured specimens contain more calcite due to the reaction of CH with atmospheric CO2. Among the air cured samples, the concrete specimen with SAP has a comparatively less carbonated product than the sample without SAP. The moisture content provided by the superabsorbent polymer (SAP) could prevent the atmospheric carbonation to certain extent. Similarly, the presence of C3S and C2S were detected more in air cured samples as the curing process was more effective in water cured specimens.

B. Microstructural Analysis by Nitrogen Adsorption

The pore structure characterization of HPC specimens containing an internal curing material was studied by means of nitrogen adsorption isotherms at -196 °C. The details of adsorption-desorption isotherm and BET surface area calculated based on the data obtained from gas adsorption experiments are discussed in this paper. Tests were conducted on solid chips of concrete specimens with/without super absorbent polymer cured under water/air for 28 days. The samples were subjected to degassing under vacuum to remove all physically adsorbed materials from the adsorbent surface before analysis, and they were weighed before and after degassing/outgassing [23, 24]. The multilayer surface adsorption model developed by Brunauer, Emmett and Teller (BET) [28, 29], an extension of Langmuir theory [30] for monolayer to multilayer adsorption was used to compare the surface areas of different samples accessible to gas molecules (Table I).

The adsorption-desorption isotherms of concrete specimens (Control and Sample with SAP) after 28 days of curing under water and air are shown in Fig. 4. The shape of the nitrogen adsorption isotherms of all the samples represent type II isotherm with H3 hysteresis according to IUPAC classification loop [31], characteristics of mesoporous and macroporous materials with limited uptakes through narrow slit pores. These kinds of isotherms are generally formed by the samples with monolayer adsorption followed by multilayer adsorption at 'point B' in Fig. 4. The slow rise of the isotherm observed after 'point B' is due to the increase in the thickness of the adsorbed layer. However, the sudden increment of the isotherm after 'point D' is due to the well-known capillary pore condensation phenomenon [29]. The N_2 adsorption isotherms showed the samples with SAP (C35SAP) have higher adsorption capacity than control samples (C35) at higher relative pressures. This clearly indicates that the incorporation of internal curing agent (SAP) increased the porosity by generating large mesopores in these concrete specimens [22].



Figure 4. Nitrogen sorption results at -196 °C for concrete specimens cured under water and air for 28 days.

 TABLE I. BET SURFACE AREA (M²/G) OF CONCRETE SPECIMENS

 CURED UNDER WATER AND AIR FOR 28 DAYS.

Curing Condition (28 days)	Control (C35)	Sample with SAP (C35SAP)
Water	5.5698	7.1905
Air	2.8889	6.2301

Even though the BET surface area of the samples with SAP (C35SAP) is higher than those without SAP due to the formation of more hydration products, larger mesopores formed in the samples with SAP make them to adsorb more gas molecules, especially at high relative pressures. Among water and air cured samples, water cured samples showed higher BET surface area due to the formation of more hydration products [32, 33].

C. FT-IR Analysis

FT-IR transmission spectra were measured by Attenuated Total Reflection (ATR) technique in the scan range of 400–4000 cm⁻¹ for all the concrete samples after 28 days of hydration. Samples absorb IR radiation of definite wavelength depending on the chemical nature of the molecular bonds present. FT-IR can be used to study the vibrational nature of bonds present in amorphous as well as crystalline samples. Fig. 5 shows the FT-IR spectra of concrete specimens recorded after 28 days of curing under water and air conditions.



Figure 5. FT-IR spectra of OPC, Mix-1 and Mix-2 samples after 28 days of curing in water and air.

The spectra contain two small peaks nearly at 3682 and 3642 cm^{-1} along with a broad peak centred at 3402 cm^{-1} . The bands at 3682 and 3642 cm⁻¹ are due to metalbonded hydroxides, while the broad band centred at 3402 cm⁻¹ is due to symmetric and asymmetric stretching vibrations (v1 and v3) of O-H adsorbed water molecules present in the concrete samples. The band at 3682 cm^{-1} is attributed to the OH from the Ca(OH)₂. The bending vibrational bands of water molecules were found at 1637 cm⁻¹. The peak intensity of the broad peak centred at 3402 cm⁻¹ was highest for the sample with SAP cured under water conditions. This clearly showed the presence of more water content in these samples; whereas the lowest peak intensity of the broad peak at 3402 cm⁻¹ for the control sample cured under water conditions signifies the effective hydration in these samples after 28 days. The asymmetric stretching vibrations (v3) of carbonate observed at 1412 cm⁻¹ due to the formation of CaCO₃ by the reaction of Ca(OH)2 with CO2 present in the atmosphere. The intensity of this band is closely related to the ratio and extent of carbonation [34, 35]. The highest peak intensity of this band observed for C35-A and C35SAP-W clearly indicates that these samples have undergone more carbonation than the rest of the specimens. The weak shoulder band at 875 cm⁻¹, due to the out-of-plane bending vibrations of CO32- shows the lowest degree of carbonation for C35-W. The same performance could be observed for C35-A and C35-W samples under XRD analysis.

The sulphate absorption bands (S-O stretching vibrations) at 1142 cm⁻¹ in the OPC disappeared during cement hydration. Only a shoulder peak is observed in this region. The gypsum reacts with aluminate and ferrite phases present in the cement to form Aft phases during the hydration process. These Aft phases react further with aluminates and ferrites to form Afm phases in the early ages. These phases remain inactive and no more changes are observed for these bands after the initial few hours of the cement hydration [36]. The strong bands that appeared at 920, 517 and 446 cm⁻¹ in OPC underwent changes on hydration. The asymmetric stretching (v3) vibration band of Si-O at 920 cm⁻¹ in dry cement shifted towards a higher wavenumber (954 cm⁻¹) after cement hydration. Also, the relative intensities of Si-O out-ofplane bending vibrations (v4, 517 cm⁻¹) and in-plane bending vibrations (v1, 446 cm⁻¹) decreased drastically after 28 days of hydration indicating the polymerization of the crystalline silicate (SiO₄⁴⁻) units to amorphous Si-O polymeric gel. The intensities of the peaks at 954 cm⁻¹ are highest for the samples with SAP (C35SAP-W and C35SAP-A). This was due to the formation of more C-S-H in these samples by silicate polymerisation [37, 38].

IV. CONCLUSIONS

The effects of superabsorbent polymers on the microstructural properties of hardened concrete after 28 days of curing under water and air was investigated by X-ray diffraction, Nitrogen sorption and FT-IR analysis. The X-ray diffraction analysis showed the presence of more carbonated products in air cured samples. The

presence of SAP increases the amount of calcium hydroxide formed in concrete specimens indicating the internal curing properties of SAP to enhance the cement hydration. The higher gas adsorption capacity of specimens with ICMs indicates that the total porosity increases with the incorporation of SAP. The FT-IR spectra also showed the presence of more carbonated products in air cured samples along with the shift of asymmetric stretching (v3) vibration band of Si-O approximately 50-60 cm⁻¹ towards higher wavenumber after cement hydration. The silicate polymerization was enhanced by the presence of SAP molecules as the maximum intensity of the peaks at 954 cm⁻¹ (Si-O asymmetric stretching) was observed for the samples with SAP (C35SAP-W & C35SAP-A). Thus, the presence of SAP in HPC increases the amount of cement hydration products at the expense of total porosity.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

AUTHOR CONTRIBUTIONS

The authors confirm contribution to the paper as follows: Concept design, concrete specimen preparations and SAP absorption studies: J. Chakkamalayath, Z. Awadh, D. Dashti, A. Joseph. Microstructural studies: A. Joseph, Z. Awadh, D. Dashti, J. Chakkamalayath. Analysis and interpretation of results: A. Joseph, J. Chakkamalayath, Z. Awadh, D. Dashti. Draft manuscript preparation: A. Joseph, Z. Awadh, D. Dashti, J. Chakkamalayath. All authors reviewed the results and approved the final version of the manuscript.

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