

HYDRATION AND MICROSTRUCTURE OF BLENDED CEMENT WITH SODIUM POLYSTYRENE SULFONATE

#WEIFENG LI*, SUHUA MA*, YUEYANG HU*, XIAODONG SHEN*, **

*College of Materials Science and Engineering, Nanjing Tech University, Nanjing 210009, China

**State Key Laboratory of Materials-Oriented Chemical Engineering

#E-mail: yc982@126.com

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Polystyrene foamed plastic wastes are a kind of environmental pollutant. It could be recycled in cement industry as a chemical agent. In this paper, the effects of sodium polystyrene sulfonate (SPS) on the hydration and microstructure of blended cement were investigated by calorimetry, X-ray diffraction (XRD), scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP). SPS slightly delayed the hydration of alite and decreased its hydration degree. SPS did not change the phase compositions during hydration. SPS changed the morphology of ettringite (AFt) and decreased the pore volumes and the sizes of pores.

INTRODUCTION

Concrete is a widely used structural material. With the increasing requirements for concrete durability and performance, new types of chemical additives have been developed, including superplasticizers (SPs). Over the past few decades, significant progress has been made in the application of SPs [1-4]. SPs play increasingly important roles in concrete. SPs are adsorbed on cement particles, providing the possibility of a better dispersion of cement particles [5]. SPs include lignosulfonic acids (LSs), melamine formaldehyde sulfonic acids (SMFs), naphthalene formaldehyde sulfonic acids (SNFs) and polycarboxylic acids (PCs) [5, 6-8]. Polycarboxylic acids are the most utilized among SPs. A number of studies have examined the effects of PCs on the hydration, morphology and microstructural development of cements [9-10]. However, the price of PCs is relatively higher, compared with cements. Additionally, a number of byproducts are produced in the production of PCs.

It is well known that polystyrene foamed plastic wastes are a primary source of environmental pollution. Thus, the recycle of polystyrene foamed plastic wastes provides significant social and economic benefits. The benzene ring in the polystyrene molecule has high chemical activity. Polystyrene can be modified into a water-soluble and functional polymer by introducing functional end groups, such as sulfonic acids, carboxylic acids and hydroxyl groups, into the benzene ring [11-12]. El-Hosiny, F.I., et al. [13] investigated the effect of sodium polystyrene sulfonates on the mechanical and physico-

chemical properties of blended cementitious pastes. It did not affect the phase composition of the blended cement hydration products. Using microelectrophoresis and UV-absorption techniques, Andersen, P.J., et al. [14] showed that sulfonated polystyrenes had larger negative ZP values and higher dispersibility, compared with sulfonated naphthalene and sulfonated melamine. Our research found [15] that 0.04 % SPS increased the compressive strengths by 19 % and 8 % at 3 d and 28 d respectively, compared to the blank cement.

In this paper, it was investigated systematically on the effects of SPS on the hydration and microstructure development of blended cement. Its aim is to provide a theoretic guide for the recycle of Polystyrene foamed plastic wastes.

EXPERIMENTAL

Materials

In this paper, the blended cement was obtained from a cement company in China. The blended cement was made of 55 % Portland cement clinker, 30 % fly ash, 6 % slag, 5 % limestone and 4 % gypsum. The chemical compositions of Portland cement clinker are shown in Table 1. SPS was added at 0.01 %, 0.03 %, 0.05 %, 0.1 % and 0.2 % by weight of the blended cement. And the structure of SPS is shown in Figure 1. The blended cement paste was made of the blended cement and deionized water. The ratio of water to the cement was 0.4.

Table 1. Chemical analysis of Portland cement clinker used.

Chemical analysis (g/100g)	
CaO	64.80
SiO ₂	21.77
Al ₂ O ₃	4.86
Fe ₂ O ₃	3.61
MgO	1.21
SO ₃	–
K ₂ O	–
Na ₂ O	–
TiO ₂	–
Loss	1.71

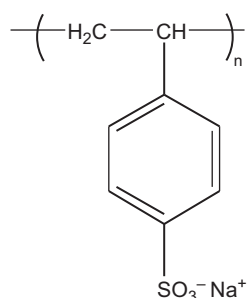


Figure 1. The molecular structure of SPS.

The SPS was prepared as follows [16]: first, waste polystyrene pellets were rinsed with 1.0 % NaOH solution and distilled water, and then dried in an oven. After that, 50 g of concentrated H₂SO₄ (95 %) with P₂O₅ catalyst was mixed in a 3-neck flask with a mixer at 40°C. Then, 10 g of polystyrene pellets was dissolved in 75 ml of cyclohexane and added to the 3-neck flask and stirred for 30 min. Subsequently, mixing was stopped in the 3-neck flask for 1 h at 40°C. After that, the 3-neck flask was placed in an ice bath, and the SPS and the cyclohexane solution were separated using a separation funnel. The remainder was washed with water several times and neutralized with NaOH. Finally, the sulfonated polystyrene solution was diluted five-fold for the experiments.

Experimental methods

Isothermal calorimetry

An 8-channel isothermal calorimeter (TAM Air; Thermometric AB, Sweden) was used to measure the hydration heat flow of the blended cement with and without SPS at 20°C. The hydration experiments were run for 3 d.

X-ray powder diffraction

The phase development was investigated on a Rigaku SmartLab 3000 A diffractometer with CuK α radiation ($\lambda = 0.154$ nm). The X-ray tube was operated at 35 kV and 30 mA. The optics configuration included a

fixed divergence slit (1/2°) and a D/teX Ultra detector. The measurements were collected using θ - θ reflection geometry. Data were collected from 10° to 70° in continuous mode.

Scanning electron microscopy analysis

For the morphology investigations, a few pieces of the cements were coated with carbon and examined using a JSM-5900 SEM operated at 30 kV.

Mercury intrusion porosimetry analysis

The porosity and pore size distribution were studied using a Quanta chrome PoreMaster GT60 mercury intrusion porosimeter capable of generating high pressures in the range of 20 psia to 20,000 psia and low pressures in the range of 1.1 psia to 20 psia. The porosimeter can be used to measure pore sizes ranging from 0.0035 μ m to 400 μ m. The pore radii were calculated according to the Washburn equation, $r = -2\gamma \cos \theta / P$, where r is the pore entry radius in which mercury is introduced, γ is the surface tension, and P and θ are the applied pressure and the contact angle of mercury with the solid, respectively.

RESULTS AND DISCUSSION

Hydration kinetics

Heat flow can characterize the hydration kinetics of cements. The heat evolution curve of typical Portland cement broadly resembles that of C₃S [17]. According to the heat flow curve for typical Portland cement, the hydration reaction is separated into three periods as follows: the (1) early, (2) middle, and (3) late stages of reaction. In the early stage, the initial peak was attributed to exothermic wetting and the formation of an AFt phase. In the middle stage, the second peak was attributed mainly to the hydration of C₃S. Figure 2a shows

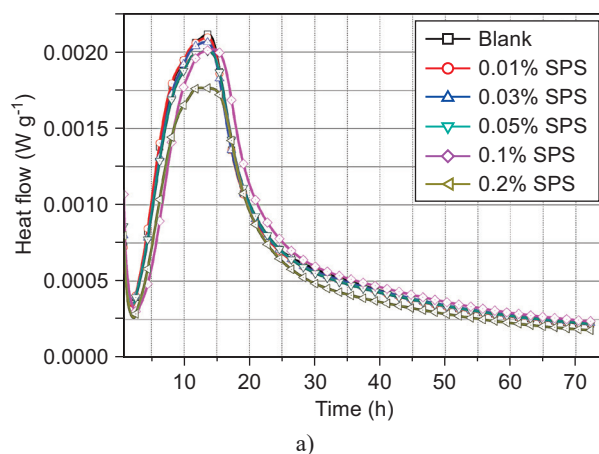


Figure 2. Heat flow curves and cumulative heat curves for cements.

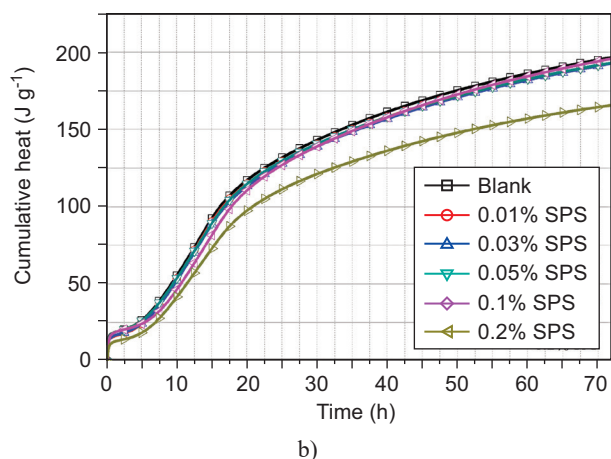


Figure 2. Heat flow curves and cumulative heat curves for cements.

that SPS did not significantly change the hydration kinetics for the blended cement. However, as the SPS dosage increased, the hydration rate of C_3S decreased. The second exothermic peak moved slightly to the right for the blended cement with 0.1 % and 0.2 % SPS. Setting takes place during an acceleratory period [17]. These results indicated that a large amount of sulfonated polystyrene will delay the hydration of C_3S and prolong the setting time.

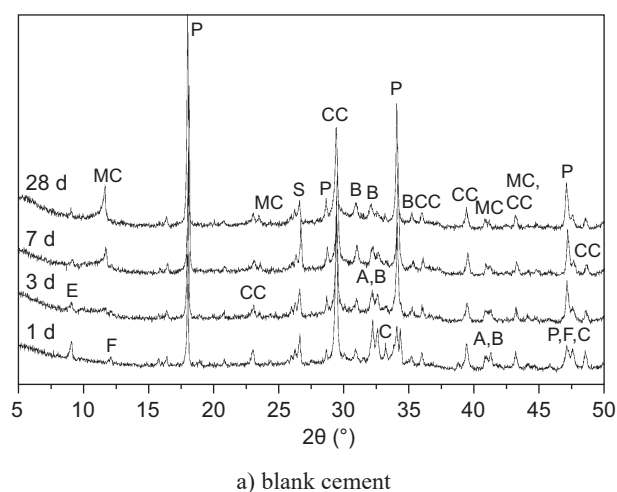
The cumulative heat was lower for the blended cement with 0.2 % SPS (see Figure 2b), compared to the other cements. With the ongoing hydration, the cumulative heat difference increased between the blended cement with 0.2 % SPS and the other cements.

Development of hydration products

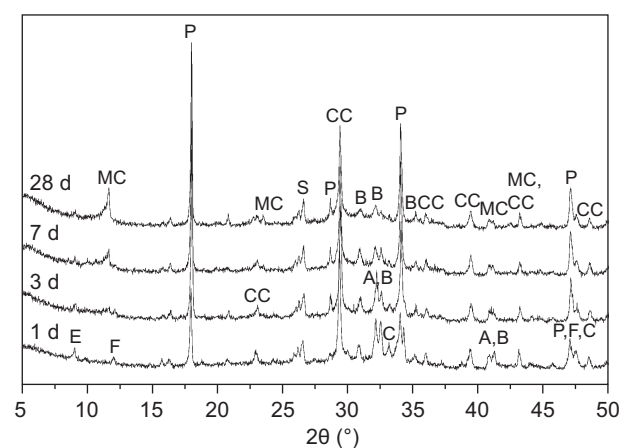
To investigate the effect of SPS on the development of hydration products, the hydration of the blended cements with and without SPS was monitored by XRD.

The XRD patterns are shown in Figure 3 for the blended cements with 0.05 % SPS and without SPS hydrated for different ages. As reported by Copeland L.E., et al. [18], gypsum was no longer detectable after 1 d (see Figure 3a), and the cement phases were consumed at different rates. The ratio of belite to alite steadily increased, and after 28 d, little or no alite, aluminate and ferrite phases were detectable. The calcite and SiO_2 were also increasingly less detectable with the ongoing hydration for the blank cement. At 1 d, the principal products were AFt, portlandite and C–S–H. C–S–H was not detected due to its poor crystallinity. When the blank cement was hydrated for 7 d, the diffraction peak of monocarbonate appeared and increased with the hydration duration. By contrast, the AFt content gradually decreased.

SPS did not change the assemblage of the phases for the cement pastes at the same hydration ages (Fig. 3b). These observations were similar to those for Na-polystyrene sulfonate reported by El-Hosiny, F.I., et al. [13]. However, SPS affect the formation rate of AFt and monocarbonates (see Figure 4). At the early stage, the AFt content was lower for the blended cement with SPS, compared with the blank cement. The AFt content decreased for all samples with ongoing hydration and disappeared by 7 days. Monosulfoaluminate was not observed in the XRD pattern. At the same time, monocarbonate formed and increased in all samples due to the continuous hydration. The monocarbonate content was also lower for the blended cement with SPS. However, it was difficult to determine the mechanism by which the monocarbonate was formed, i.e., by the reaction of C_3A and $CaCO_3$, the main mineral in limestone, and/or by the reaction of AFt, C_3A and $CaCO_3$. It was previously reported [19] that limestone could stabilize AFt and react with the remaining aluminates to form a combination of mono- and hemicarbonates for ordinary Portland cement–fly ash–limestone systems.



a) blank cement



b) blended cement with 0.05 % SPS

Figure 3. The XRD patterns of blank cement hydrated for 1d, 3d, 7d and 28d; a) blank cement, b) blended cement with 0.05 % SPS.

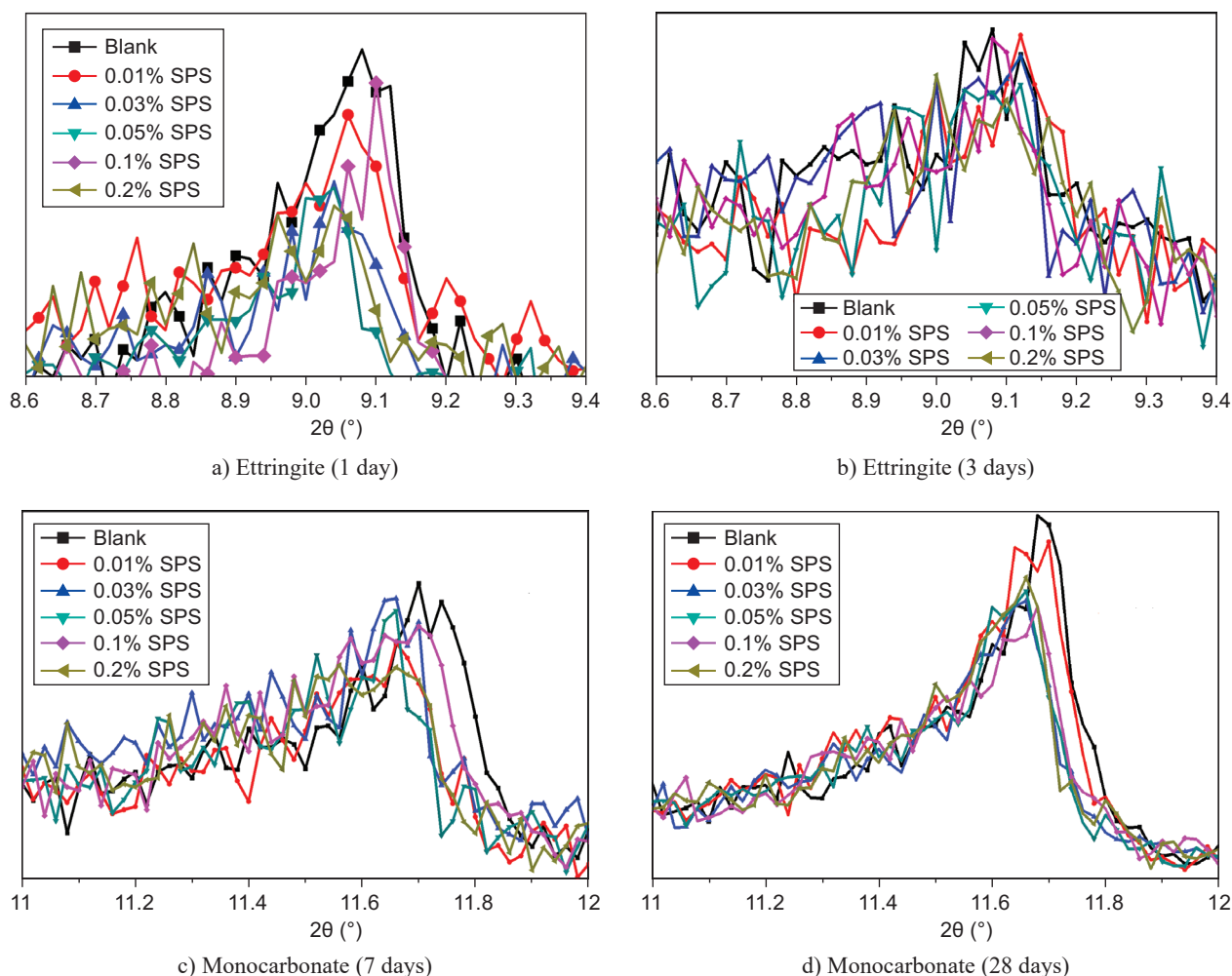


Figure 4. The characteristic peak of ettringite and monocarbonate for cements hydrated for different ages.

Morphology of hydrates

To investigate the effect of SPS on the morphology of the hydrates, a slice of blended cements without and with 0.05 % SPS hydrated for 1 d was visualized by SEM. The images are shown in Figure 5. At the early stage,

a large amount of monosulfoaluminate/monocarbonate formed apart from the AFt for the cements without and with 0.05 % SPS (see Figure 5a, b). However, the needle shape of AFt phase in cement paste blended with 0.05 % SPS was more elongated compared with that in reference sample (Blank) (see Figure 5c, d).

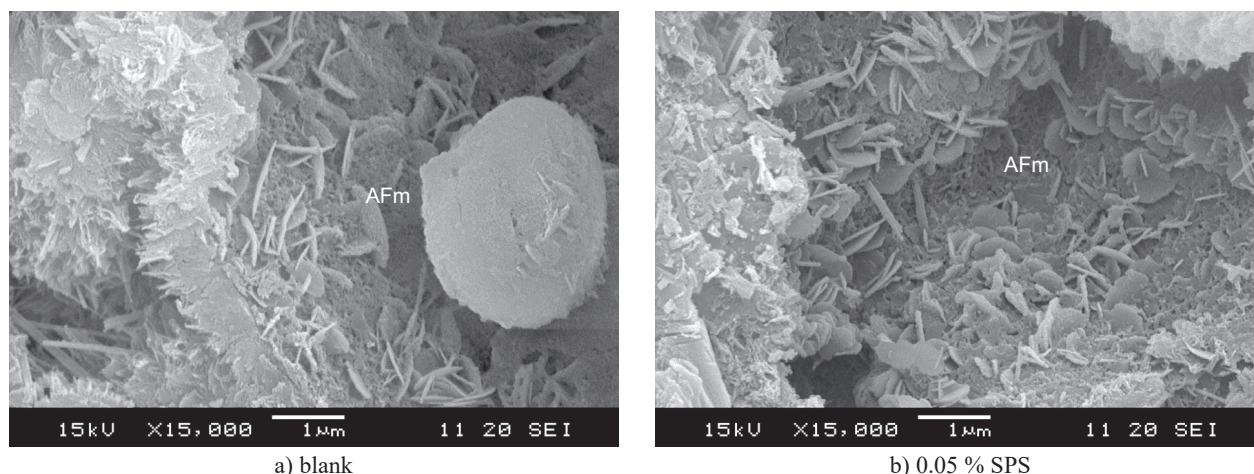


Figure 5. SEM pictures for the blank blended cement and blended cement with 0.05 % SPS hydrated for 1 d. (Continue on next page)

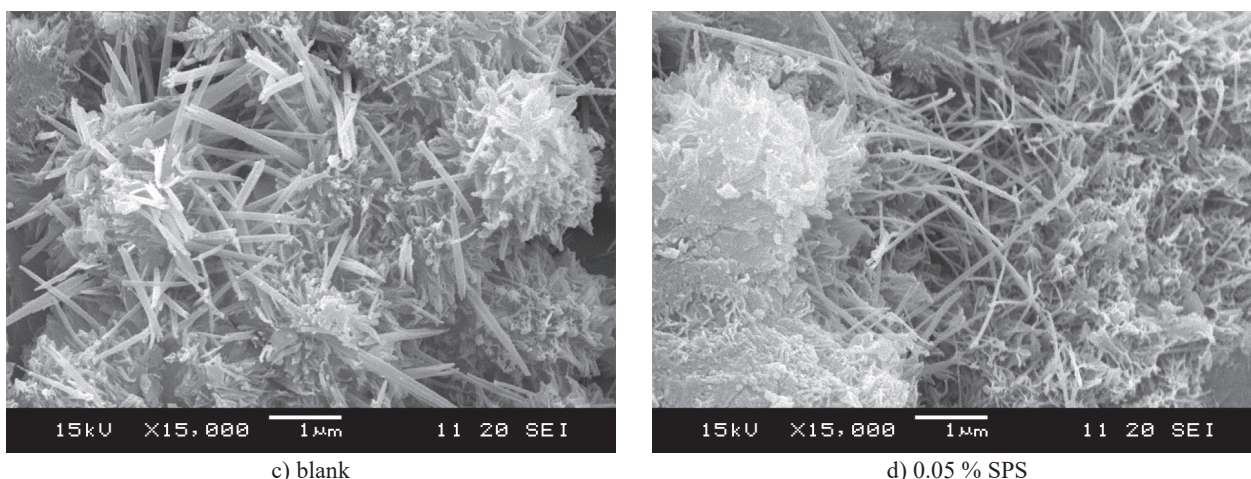
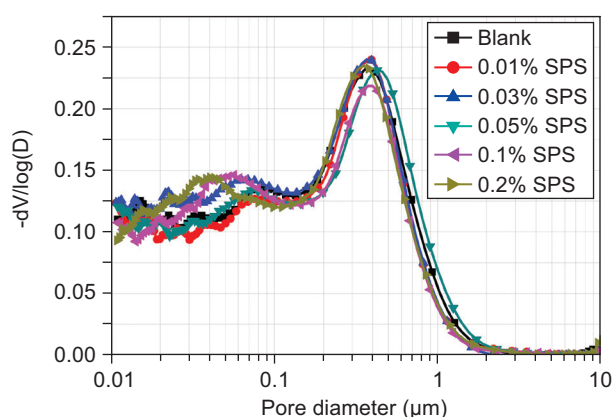


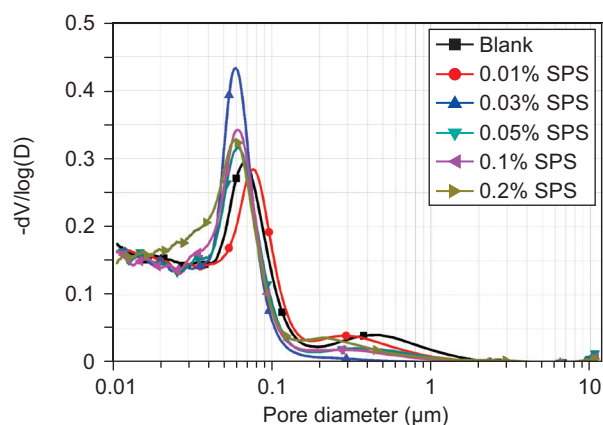
Figure 5. SEM pictures for the blank blended cement and blended cement with 0.05 % SPS hydrated for 1 d.

Pore distribution

The properties and durability of materials based on cements are dependent on its porous properties. The pore distribution is shown in Figure 6 for all cements hydrated for 3 d and 28 d. At the early stage (see Figure 6a), the pores were divided into two groups based on



a) 3 d



b) 28 d

Figure 6. Pore size distribution for cements hydrated for 3 d and 28 d.

their pore size: from 0.01 μm to 0.1 μm and from 0.1 μm to 2 μm . The presence of SPS did not change the pore distribution in the range of 0.1 μm to 2 μm . However, SPS decreased the pore sizes of the smaller pores. At 28 d (see Figure 6b), the pores sizes significantly decreased, compared for the cement pastes hydrated for 3 d. A large distribution of 0.01 μm to 0.1 μm pores and a small distribution of 0.1 μm to 1 μm pores were observed. SPS decreased the pores size and the cumulative volumes of pores with 0.1 μm to 1 μm and. It is well known that the pores in the range of 0.01 μm to 2 μm affect the strength and permeation of materials based on cements. Hence, the increased strength of cements containing SPS may be related to the decreased pore volumes and sizes.

CONCLUSIONS

Based on the presented results, large amounts of SPS delayed and decreased the hydration of alite. It did not change the hydration reaction mechanism for the cement clinker-gypsum-fly ash-limestone-slag system. SPS did not change the phase compositions for the blended cement hydrated for 1 d, 3 d, 7 d and 28 d but modifying the morphology of Aft. For this system, monocarbonate formed at 7 d due to the reaction of CaCO_3 from the limestone. SPS decreased the pore sizes and volumes at 3 d and 28 d.

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