

Hydration Characteristics of Super Sulphated Cement with Different Fineness

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Abstract—The various periods mechanical performance of super sulphated cement(SSC) with different fineness are investigated in this paper. The hydration exothermic rate, hydration products and morphology of SSC are tested with differential scanning calorimetry(DSC), X-ray diffraction analysis(XRD) and scanning electron microscopy(SEM), separately. Experimental results show that sample particles in turn become finer followed by No.SSC-1, SSC-2 and SSC-3, the compressive strength of SSC-3 and SSC-2 are significantly higher than SSC-1 with same ages, which are 11.7MPa and 5.8MPa higher than SSC-1sample at 3days, and, 19.9MPa and 17.5MPa higher than SSC-1sample at 28 days, respectively. With the increasing of specific surface area(SSA), the duration of induction period was shortened nearly more than 10 hours, the amount of ettringite phase and C-S-H gel also significantly increased, which makes SSC paste more compact.

Keywords-super sulphated cement (SSC); particle size distribution; hydration exothermic rate; ettringite phase; C-S-H gel

I. INTRODUCTION

SSC is a kind of hydraulic cementitious material which is produced by the activation of alkali and sulfate in combination on slag latent activity; it is a kind of low energy eco-cement which has lower energy consumption and less CO₂ emissions. Current research on SSC has largely focused on physical and mechanical properties of SSC, activity of industrial waste in SSC, hydration product analysis about SSC system and so on[1~4]. But, few researchers are engaged in comparative study of hydration rate, hydration product phase and morphology of SSC with different fineness.

To explore hydration characteristics of SSC with different fineness, compressive strength, hydration rate, hydration product morphology of SSC pastes are studied in this paper.

II. MATERIALS AND METHODS

Based on the same weight ratio, ordinary Portland cement clinker, slag and gypsum were used to prepare SSC, which were numbered SSC-1, SSC-2 and SSC-3, and represented SSC with SSA 342m²/kg, 454m²/kg and 543m²/kg, respectively. The chemical compositions and particle size distribution of SSC with different fineness were shown in Table 1 and Table 2.

TABLE I. CHEMICAL COMPOSITION OF SSC (wt, %)

No.	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	SO ₃	K ₂ O	CaO	Fe ₂ O ₃
SSC	0.218	5.187	11.430	26.420	0.326	12.270	0.588	41.020	1.244

TABLE II. PARTICLE SIZE DISTRIBUTION OF SSC (μm, %)

No.	SSA	D10 ^a	D25	D50	D75	D90
SSC-1	342m ² /kg	2.11	4.30	12.19	24.84	33.99
SSC-2	454m ² /kg	1.31	2.70	6.15	13.46	20.80
SSC-3	543m ² /kg	1.09	2.33	4.99	10.81	17.48

a. the percentage of particles which are smaller than 10 microns.

SSC pastes were cast in 40mm×40mm×40mm moulds, and cured in standard conditions (20±1 °C, RH 95%). The water to binder ratio (w/b) for all samples was 0.4.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

A. Compressive Strength of SSC Pastes

Figure 1 showed compressive strength test results of SSC pastes. From Figure 1, it can be seen that the smaller the particle size of SSC, the greater the compressive strength of SSC pastes. SSC-3 and SSC-2 with the compressive strength 26.6MPa and 17.7MPa at 3 days, 50.7MPa and 48.2MPa at 28 days, is 11.7MPa and 5.8MPa higher than SSC-1sample at 3days, and, 19.9MPa and 17.5MPa higher than SSC-1 compressive strength at 28 days; 90 days compressive strength of SSC-2 is closer to SSC-3, there are all 10MPa higher than the compressive strength of SSC-1.

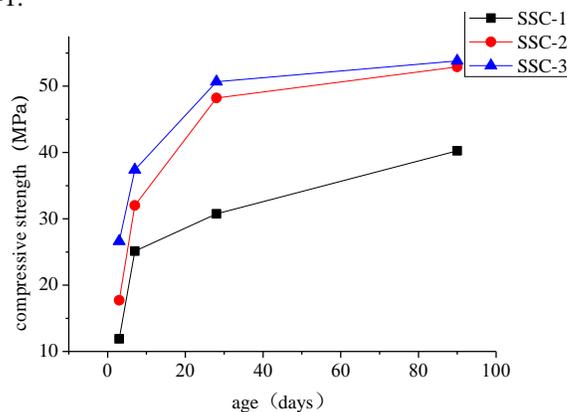


Figure 1. Compressive strength of SSC pastes

B. Hydration Exothermic Rate and Hydration Heat Curves of SSC with Different Fineness

Hydration exothermic rate and hydration heat curves of SSC are shown in figure 2 (a) and (b) below. As can be seen from figure 2 (a), the early stage hydration of SSC is divided into five periods, the pre-induction, induction, acceleratory, deceleration and stabilization periods, which are similar to hydration process of Portland cement. By comparative analysis of hydration process on different samples, it can be clearly seen that the duration of induction period was shortened nearly more than 10 hours and the occurrence time of the second exothermic peak was significantly advance with decrease in particle size of SSC; As seen from figure 2 (b), with the significantly increasing of SSA, SSC samples hydration heat was also significantly increased, which indicate the acceleration of early hydration reaction. These results revealed that the SSA increasing would contribute to the early hydration rate of SSC.

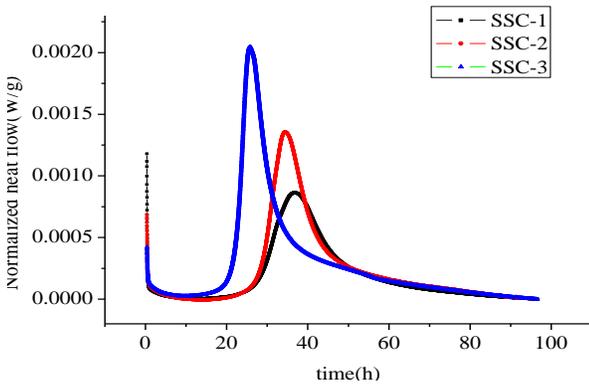


Figure 2(a). Hydration exothermic rate of SSC

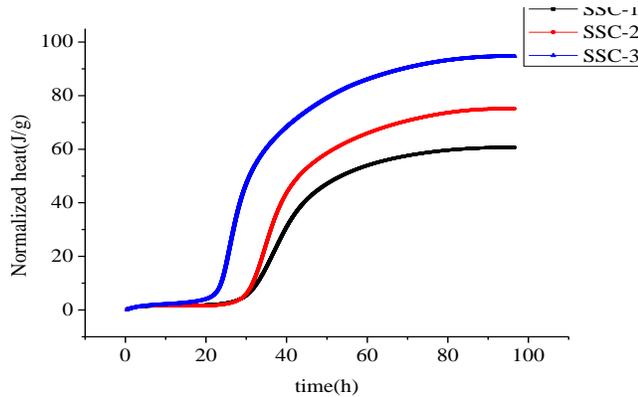


Figure 2(b). Hydration heat curves of SSC

C. Hydration Products of SSC with Different Fineness

Figure 3 (a), (b), (c) and (d) show XRD and SEM test results of SSC samples with four age periods. As can be seen, with the decrease in particle size of SSC samples, the amount of ettringite phase basically increases by turns. And, earlier the age is, more significant the characteristic peak of ettringite peaks would be; moreover, gypsum peak is gradually weakened as SSA increasing at same age. There's essentially no gypsum characteristic peak for SSC-2 after 7

days, so the same situation with SSC-3 after 3 days. These indicated that decrease of grinding fineness would be beneficial to promote SSC hydration, especially early hydration of SSC.

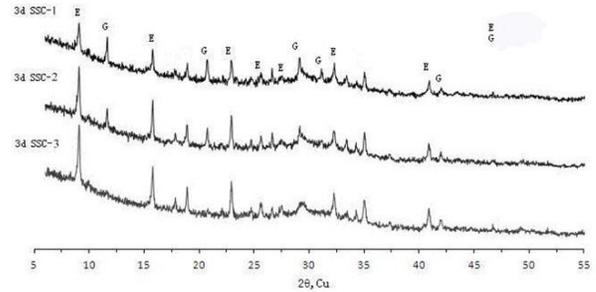


Figure 3(a). XRD pattern of SSC hydration products(3d)

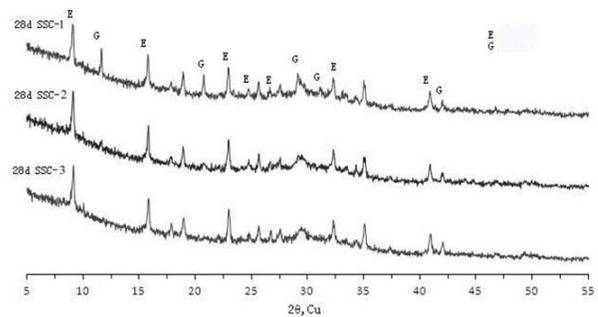


Figure 3(b). XRD pattern of SSC hydration products(7d)

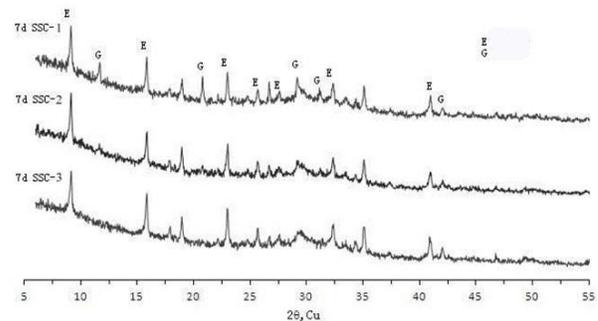


Figure 3(c). XRD pattern of SSC hydration products(28d)

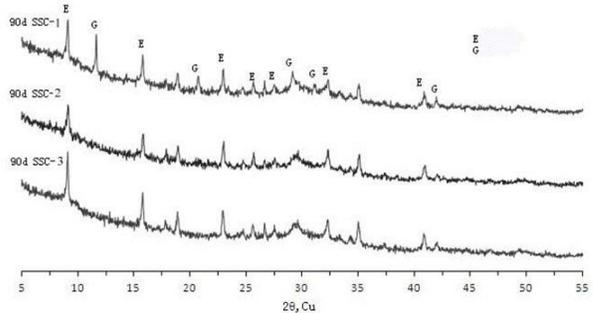


Figure 3(d). XRD pattern of SSC hydration products(90d)

(E represents ettringite, G represents plaster)

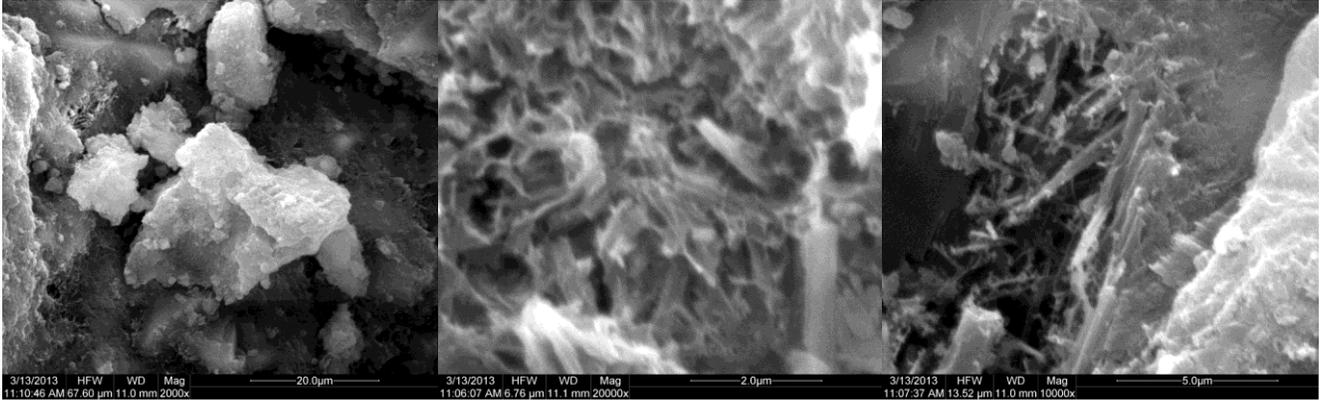


Figure 4(a). Morphology of SSC-1 pastes at 90 days

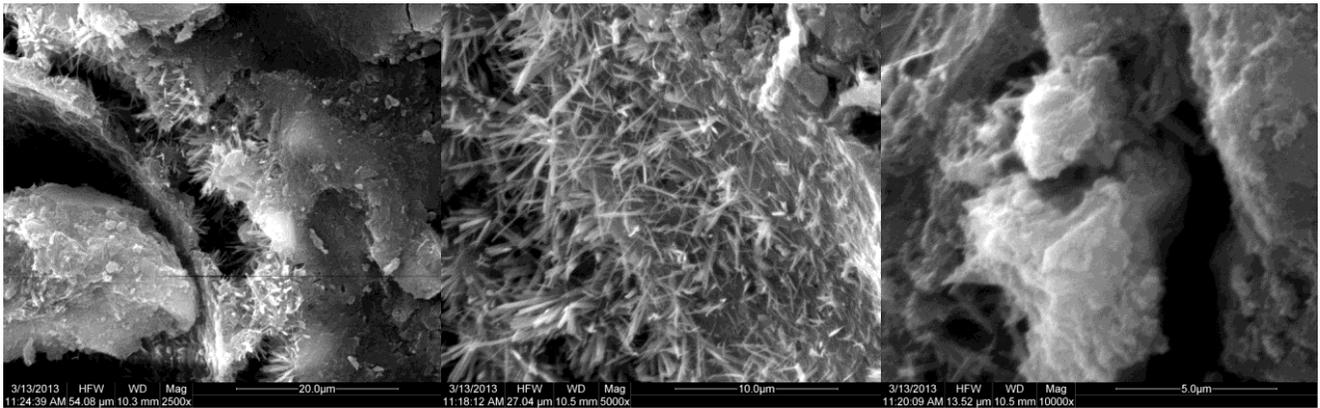


Figure 4(b). Morphology of SSC-2 pastes at 90 days

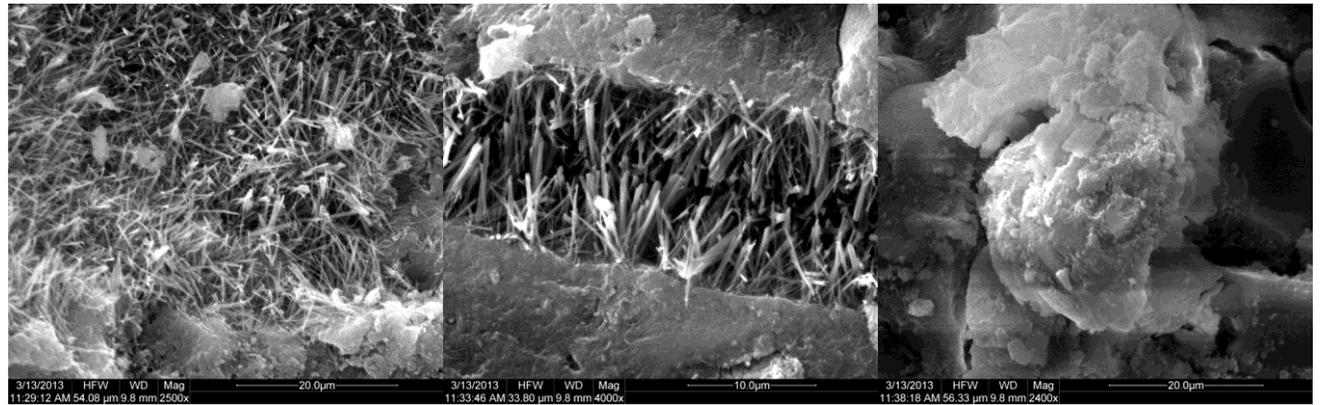


Figure 4(c). Morphology of SSC-3 pastes at 90 days

Combine with morphology figure 4 (a), (b) and (c), there are a lot of fine needle-like or rod-like column ettringite crystals in SSC hydration products, which intertwined with the fibrous calcium silicate hydrate gel(C-S-H), and form a continuous network structure throughout the entire space. Both components of ettringite crystals and C-S-H together make up skeleton structure of SSC paste. And it can be clearly seen that fine needle hydration ettringite crystals and C-S-H gel continuously filled in some cracks or pores, gradually remedy the paste structural defects and improve pore structure distribution of SSC pastes, these are benefit to

enhancing mechanical properties. Most ettringite crystals are fibrous; some are fine needle or columnar. These may be closely related to changes of alkalinity in SSC system.

D. Hydration Mechanism of SSC with Different Fineness

From above experimental results, the main hydration products in SSC system are ettringite, C-S-H gel and partially unhydrated gypsum crystals. The formation of ettringite decides the early strength development to certain extent, C-S-H gel is the core contributor of later strength and it determines the long-term strength development to a

great extent. Based on permeation law, chemical effects and nonmaterial theories, SSC hydration mechanism of different fineness can be explained as follows.

Firstly, hydration rate depends on the diffusion rate of water molecules passing through hydration layer[5~7]. as in

$$X = 2 \times t^{(1/4)} \quad (1)$$

x (μm) is the depth hydration, t (days) is the hydration time.

According to the penetration law, 28d hydration degree of 32 μm particles approximately 37%, the smaller the SSC particles, the higher the hydration degree, large particles only can fill some pores. Therefore, the particles fineness of SSC plays a decisive role in the hydration system. The particles size distribution of SSC are listed in table 2, it can be seen that, particle sizes of No. SSC-1, SSC-2 and SSC-3 are finer in turn, which is beneficial to the development of paste strength.

Furthermore, according to mechanochemical effect[8,9], SSA of SSC increase with the decreasing of particle size during mechanical milling, mechanical forces also destroyed the crystal structure in the meantime, SSC activity can be improved to some extent due to structural distortion and increasing of internal and surface defects; Furthermore, from the energy standpoint, mechanical energy would partially converted to surface and internal energy, which can increase total energy of solid particles, then, increases reactivity of SSC; Lastly, based on nanomaterials theory[10,11], gargantuan SSA of SSC makes the increasingly surface atoms and severe mismatch of valence, the rapid increase of surface energy makes highly active surface atoms, which are easily combine with other atoms, all these are benefit to accelerate hydration process of SSC.

Therefore, with the decrease of particle fineness, SSC hydration reaction rate is accelerated, overall microstructure become denser; Strength increases with decrease particle size.

IV. CONCLUSIONS

- (1) SSC-3 and SSC-2 (SSA of 454 m^2/kg and 543 m^2/kg) with the compressive strength 26.6MPa and 17.7MPa at 3 days, 50.7MPa and 48.2MPa at 28 days, is significantly higher than SSC-1 (SSA of

342 m^2/kg) with same ages.

- (2) With decrease of particle size, the duration of induction period was shortened nearly more than 10 hours, hydration process has obviously accelerated, and these are in agreement with early strength test results.
- (3) Results from XRD and SEM reveal that gypsum peak is gradually weakened as SSA increasing at same age, and the amount of ettringite phase and C-S-H gel also significantly increased, which makes paste structure denser.

REFERENCES

- [1] Li Lei, Zhao Qinglin, He Tao, Zhou mingkai. Study on performance of Super Sulphated Cement masonry mortar [A]. The third nationwide academic symposium on commercial mortar [C]. Wuhan, 2009, pp.51-54. (In Chinese)
- [2] Li Lei .Research of Enhance Mechanism and Application on Supersulphated Cement Using Metallurgical Slag [D]. Wuhan university of Technology, 2010. (In Chinese)
- [3] V. Glukhovskij., Y. Zaitsev, V. Pakhomow. Slag-alkaline Cements and Coneretes. Structures, properties, technological and economical aspects of the use, Silicates. Vol.48 Ind., 1983, pp. 197–200.
- [4] Zhao Qinglin, Zhou Mingkai. Research and Application of Supersulphated Cement in German[J]. Cement Guide for New Epoch, 2008, pp. 5–10. (In Chinese)
- [5] S. Tsvilis, S. Tsimas, A. Benetatou, E Haniotakis. Study on the contribution of the fineness on cement strength[J]. ZKG, 1990(1): 26.
- [6] I. B. Celik. The effects of particle size distribution and surface area upon cement strength development[J]. Powder Techn, Vol.188 2009, pp. 272-276.
- [7] G. Frigione, S. Marra. Relationship between particle size distribution and compressive strength in portland cement [J]. Cem Concr Res, Vol. 16. 1976, pp. 113-128.
- [8] Gaffet Eric, Bernard Frederic, Niepce Jean Claude, et al. Some recent developments in mechanical activation and mechanochemistry[J]. J Mater Chem, 1999, pp. 305-314.
- [9] Li Jingxian, Wu Jiqu, Huang Kangming. Mechano-chemical effects in inorganic non-metals materials preparations[J], Journal of the Chinese ceramic society, Vol.30. 2002, pp.152~154. (In Chinese)
- [10] Li Xiufen, Liu Hongbo, Wang Fei. The summary of application of nanometer material in cement industry[J], China Building Materials Science & Technology, 2008, pp.70~73. (In Chinese)
- [11] Xiang Gao, Qinghua Li, Shilang Xu. Compressive strength and flexural properties of high performance nano-binder cementitious composites[J]. Applied Mechanics and Materials, Vol. 275-277 2013, pp.2064-2068.