7th International Conference on the Durability of Concrete Structures
20-22 May 2022
University of Jinan, Jinan, Shandong, China

Improving properties of supersulfated cement by regulating its physiochemical features through nanoSiO_2-modification

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ABSTRACT

Supersulfated cement (SSC) has been known as a low-carbon cementitious materials due to its low-clinker requirement but high-slag consumption. However, the slow property gain rate, especially at the early ages, together with the long-term drawbacks introduced by the physiochemical characteristics of SSC, has primarily blocked its application. In this work, a novel property-gain regulation technique by applying nanoSiO_2 (NS) modification on the binding system was reported. Firstly, the macro-property of SSCs with NS was presented, and then the hydration features, as well as the physiochemical properties, were reported. It was found that 3 wt.% NS addition could increase the 90-day compressive strength of SSC to 100%, and the critical pore threshold value can be reduced by an order of magnitude. Quantitative analysis results showed that the modification of the chemical compositions and the variation of the resulting binders contribute to these significant changes. All these results highlighted a novel technique of developing a low-carbon cementitious binder with good performance through nano-engineering.

1. INTRODUCTION

Supersulfated cement (SSC) consists of alkali activators (cement, CaO, or portlandite, <5wt.%), sulfate (gypsum, 10-25 wt.%), and slag (70-85 wt.%) [1-3]. Due to its low clinker/cement ratio, SSC has been one of the most important low-carbon cement. However, it is because of the high slag content of SSC, its early strength development rate is quite slow, which has been one important issue limiting the application of this promising materials.

Methods such as increasing hydration temperature, lowing the fineness of slag, lowing the water cement ratio, and so on [4, 5], have been proposed to promote the hydration of slag, however, the enhancing effect is far from what one expected. Recently, sodium lactate has been found to increase the performance of SSC with slag of low activity [6, 7]. The authors proposed that the chelation effect of lactate on the surface of slag could be one possible reason, and the chelated structure had the effect of weakening the oxygen bridges which bind the surface silicon ions to the underlying silica network. It seems that the important role of sodium lactate could be accelerating the dissolution. Indeed, the hydration process of slag, dissolution of slag and the precipitation of its hydration products (ettringite and C-A-S-H), is a critical factor determining the performance development. The regulation of the hydration of silicate and aluminate from slag could be a right route to improve the performance of SSC.

NanoSiO_2 (NS) has been a popular material in cement-based materials, due to its ultrafine size, high pozzolanic reactivity, seeding effect and so on [8, 9]. Recently, NS has been found to regulate the hydration of silicate and aluminate in a significantly way: obviously accelerating the hydration of silicate, but significantly postponing (not prevent totally) the hydration of aluminate [10]. From this, one could regulate the relative reaction rate of silicate and aluminate (reaction route of slag). This study would show that the change of reaction rout of slag would significantly improve the performance development.

In this study, 0-3wt% NS was added into SSC, and the compressive strength, porosity, and chemical compositions of hardened SSC were measured to reveal the role of NS in the hydration SSC [11].

2. EXPERIMENTAL

2.1 Materials

Commercial slag and NS (7-40 nm, and a specific surface area of 380 m^2/g), Portland cement (Chinese PI 42.5), and analytical grade gypsum were used in this study. Their chemical composition is presented in Table 1. The superplasticizer from Sobute and Chinese standard sand were used as well.

Table 1. Chemical compositions of Portland cement and GGBS

	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	MgO	LOI	SSA (m^2/Kg)
Portland cement	64.39	21.88	4.31	2.56	3.47	1.72	1.42	340

GGBS	30.20	32.78	17.55	2.30	1.45	6.36	9.36	531

Table 1. Proportion of the main components of SSC (wt.%)

Samples	Clinker	GGBS	Gypsum	Limestone	NS	Superplasticizer	
						Paste	Mortar
G10	5	75	10	10	0	0	0
G10N3	5	72	10	10	3	1.5	2.5

2.2 Methods

The compressive and flexural strength of hardened SSC mortars was measured according to the Chinese standard 'GB/T 17671-1999'. The compressive and flexural strength were measured at 1, 3, 7, 28, 56, and 90 days.

The porosity of 90-days SSC were measured with MIP method (Micromertics, AutoPore IV 9500). The pressure ranges from 0.5 to 55000 psi, meaning that the pores ranging from~355 um to ~3.3 nm could be measured.

The mineral assemblage of hardened SSC was determined by XRD, which were obtained from a D8 Advance diffractometer. The 2-theta angle ranges from 5° to 80° with a step size of 0.02° and a scanning speed of 10° per minute. 20% corundum was intermixed with the sample powder with an agate mortar. Rietveld analysis was made on TOPAS 4.2 to quantify the mineral assemblage and the crystal structures used are shown in Table 3.

Table 3. Crystal structures for Rietveld analysis

Structure	ICSD code	Reference
Corundum	77810	[12]
C_3S monoclinic	94742	[13]
C_2S	963	[14]
Gypsum	409581	[15]
Ettringite	155395	[16]
Calcite	40545	[17]

3. RESULTS AND DISCUSSION

3.1 Compressive and flexural strength of SSC

Figure 1 present the influence of NS on the compressive strength of SSC. It can be seen that the early strength of normal SSC is quite week, the 3-day strength is less than 15 MPa and 90-day strength is only around 25 MPa. However, the compressive strength of SSC with NS is much higher than that without NS. Compared to the control sample, the 3-day strength of SSC with NS is increased by 35%, and the 90-day strength is increased by nearly 100%. It shows the significant enhancing effect of NS on the performance of SSC. In addition, it can be clearly seen that the enhancing effect increased with time. The phenomenon is obviously different from the effect of NS in Portland cement system and blend cement system, in which, NS mainly improves their mechanical properties at early ages (basically the first 7 days) [18].

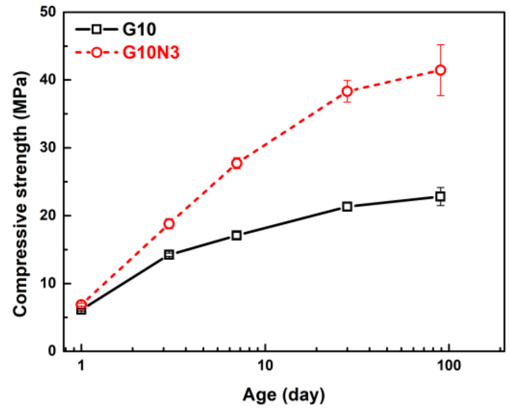

Figure 1. Compressive strength of SSC with and without nano SiO_2 as a function of time.

Figure 2 present the influence of NS on the flexural strength of SSC. Surprisingly, it seems that NS has limited enhancing effect on the flexural strength of SSC. In addition, it appears that the enhancing effect is almost constant, significantly different from its effect on the compressive strength.

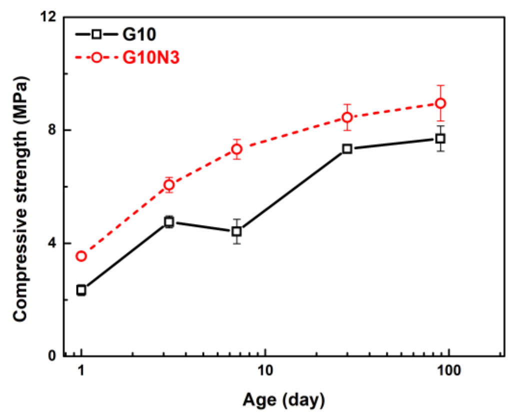

Figure 2. Flexural strength of SSC with and without nano SiO_2 as a function of time.

3.2 Porosity of SSC

Figure 3 and Figure 4 present the influence of NS on the pore structure of hardened SSC at 90 days. From Figure 3, it can be seen that the porosity of SSC is significantly reduced from 23% to 13%. The densification of micro structure is consistent with its effect on the compressive strength. From Figure 4, it can be found that the critical pore size is reduce from 72.8 nm to 6.5 nm, with a reduction of one order of magnitude. It means that NS would fill the both the large and small pores in the hardened SSC. The filling effect could the largest contributor of the compressive improvement.

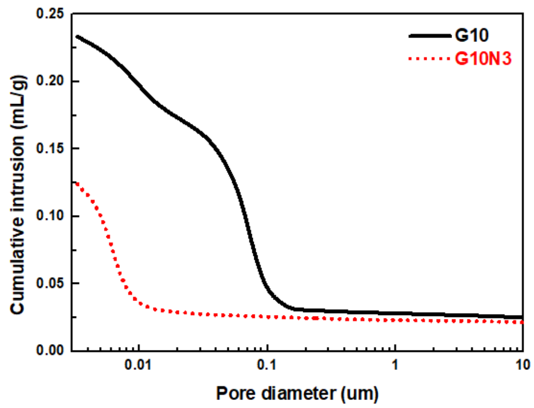

Figure 3. Porosity of SSC with and without nano SiO_2 at 90 days.

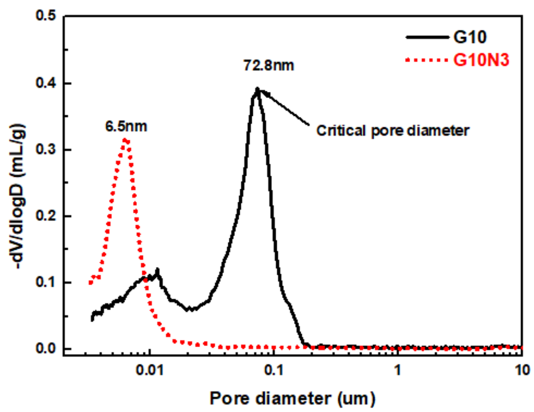

Figure 4. Pore size distribution of SSC with and without nano SiO_2 at 90 days.

3.3 Mineral assemblage of hardened SSC

The most important phases in the hardened SSC are ettringite (AFt) and calcium aluminosilicate hydrate (C-A-S-H). AFt has been considered as the main contributor of the early strength of SSC, and C-A-S-H is for the long-term strength of SSC. Therefore, their contents in the hardened SSC were quantified with the combination of XRD, TG and EDTA method. First, one can obtain the content of AFt and amorphous phases by XRD. Then, according to the hydration degree of slag, obtained by EDTA method, one can calculate the content of C-A-S-H gels by subtracting the unreacted slag from the amorphous phases.

Figure 5 presents the effect of NS on the amount of AFt and C-A-S-H gels in the hardened SSC at 28 days. It can be seen that the AFt content of SSC with NS is lower than the control sample, meaning that NS would postpone the precipitation of AFt. In addition, the amount of C-A-S-H is significantly increased by the presence of NS. This is consistent with our previous study on the system of C_3A-C_3S-Gypsum system. The regulation of NS on silicate and aluminate could be an important factor in enhancing effect of NS, including the filling effect of NS.

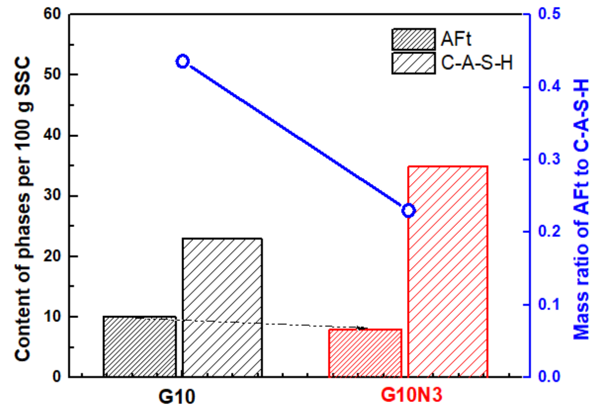

Figure 5. Amount of AFt and C-A-S-H phase in SSC with and without nano SiO_2 at 28 days.

The mass ratio of AFt to C-A-S-H (A/C) seems to be an important parameter. Since C-A-S-H has denser structure, and requires less chemical bond water, lower A/C would mean more space and water for the hydration of slag, which is important factors determining the hydration rate and hydration degree of slag.

However, the lower content of fiber-like AFt could be one reason for the limited improvement efficiency of NS on the flexural strength of SSC, since the AFt would act as microfiber in the hardened SSC pastes.

CONCLUSIONS

In this study, the influences of nanoSiO_2 (NS) on the hydration and hardening properties of supersulfated cement (SSC) was explored. The following conclusions can be drawn:

1) NS increases the compressive strength of SSC at early and late age, and the 90-day compressive could be increased by nearly 100%;
2) NS has limited enhancement on the flexural strength of SSC, probably due to the less fiber-like AFt content in the hardened SSC;
3) NS significantly densify the microstructure of SSC, reducing both the porosity and critical pore size by 70% and 91%, respectively;
4) NS could limit the hydration of aluminate and promote the hydration of silicate, regulating the hydration route of slag, and it could be one reason for the enhancing effect of NS.

ACKNOWLEDGMENTS

The authors gratefully acknowledge support from Shandong Natural Science Foundation (ZR2020YQ33), National Science Foundation of China (52102021).

REFERENCES

1. Q. Wu, Q. Xue, Z. Yu, Research status of super sulfate cement, Journal of Cleaner Production, 294 (2021) 126228.
2. A. Gruskovnjak, B. Lothenbach, F. Winnefeld, R. Figi, S.C. Ko, M. Adler, U. Mäder, Hydration mechanisms of super sulphated slag cement, Cement and Concrete Research, 38 (2008) 983-992.
3. F. Bellmann, J. Stark, T. Matschei, Hydration behaviour of sulphate-activated slag cements, Advances in Cement Research, 17 (2005) 167-178.
4. S. Liu, L. Wang, Y. Gao, B. Yu, W. Tang, Influence of fineness on hydration kinetics of supersulfated cement, Thermochimica Acta, 605 (2015) 37-42.
5. C. Angulski da Luz, H. R. D, Influence of curing temperature on the process of hydration of supersulfated cements at early age, Cement and Concrete Research, 77 (2015) 69-75.
6. Y. Zhou, Z. Peng, L. Chen, J. Huang, T. Ma, The influence of two types of alkali activators on the microstructure and performance of supersulfated cement concrete: mitigating the strength and carbonation resistance, Cement and Concrete Composites, 118 (2021) 103947.
7. R. Masoudi, R.D. Hooton, Influence of alkali lactates on hydration of supersulfated cement, Construction and Building Materials, 239 (2020) 117844.
8. M. Balapour, A. Joshaghani, F. Althoey, Nano-SiO2 contribution to mechanical, durability, fresh and microstructural characteristics of concrete: A review, Construction and Building Materials, 181 (2018) 27-41.
9. G. Land, D. Stephan, The influence of nano-silica on the hydration of ordinary Portland cement, Journal of Materials Science, 47 (2011) 1011-1017.
10. P. Hou, X. Wang, P. Zhao, K. Wang, S. Kawashima, Q. Li, N. Xie, X. Cheng, S.P. Shah, Physicochemical effects of nanosilica on C3A/C3S hydration, Journal of the American Ceramic Society, 103 (2020) 6505-6518.
11. C. Hesse, F. Goetz-Neunhoeffer, J. Neubauer, A new approach in quantitative in-situ XRD of cement pastes: Correlation of heat flow curves with early hydration reactions, Cement and Concrete Research, 41 (2011) 123-128.
12. F. Werfel, O. Brümmer, Corundum Structure Oxides Studied by XPS, Physica Scripta, 28 (1983) 92-96.
13. Á.G. De La Torre, S. Bruque, J. Campo, M.A.G. Aranda, The superstructure of C3S from synchrotron and neutron powder diffraction and its role in quantitative phase analyses, Cement and Concrete Research, 32 (2002) 1347-1356.
14. K.H. Jost, B. Ziemer, R. Seydel, Redetermination of the structure of β-dicalcium silicate, Acta Crystallographica Section B, 33 (1977) 1696-1700.
15. D.S. B.F. Pedersen, Neutron Diffraction Refinement of the Structure of Gypsum, CaSO4.2H20, Acta Crystallographica Section B, B38 (1982) 1074-1077.
16. F. Goetz-Neunhoeffer, J. Neubauer, Refined ettringite (Ca6Al2(SO4)3(OH)12·26H2O) structure for quantitative X-ray diffraction analysis, Powder Diffraction, 21 (2006).
17. S.A. Markgraf, R.J. Reeder, High-temperature structure refinements of calcite and magnesite, American Mineralogist, 70 (1985) 590-600.
18. X. Liu, P. Hou, H. Chen, Effects of nanosilica on the hydration and hardening properties of slag cement, Construction and Building Materials, 282 (2021) 122705.