Effect of Silica Fume on Early Performance of Precast Concrete with Early Strength Agents

GENG Fei[1*], *LIANG Zizhao*[1], *YANG Hangli*[1], *WU Zhongqin*[2], *ZHU Xiongwei*[2], *XU Junlun*[1]

1. College of Civil Aviation, Nanjing University of Aeronautics and Astronautics, Nanjing 211106, P. R. China;
2. Jiangsu Yuhui Housing Industry Co., Ltd, Taizhou 225300, P. R. China

(Received 20 June 2022; revised 25 July 2022; accepted 25 August 2022)

Abstract: The effect of silica fume on the early performance of precast concrete with an early strength agent was investigated. The ternary compounding technique of silica fume, fly ash and early strength agent were used to examine the compressive strength, heat of hydration, hydration products, and microstructures of the precast concrete. The experimental results showed that the optimum amount of silica fume in the precast concrete was 9%. Silica fume filled the fine pores between the cement particles. However, the cement hydration was mainly influenced by the water-to-cement ratio and cement particle size. As the hydration reaction continued, silica fume provided more nucleation sites, and the characteristic volcanic ash reaction increased both the hydration degree and hydration rate of the early strength agent doped cementitious materials.

Key words: Silica fume; concrete; premature strength; heat hydration; pore structure

CLC number: TU528.31 **Document code:** A **Article ID:** 1005-1120(2022)S-0090-08

0 Introduction

The strength development of precast concrete is closely related to the maintenance temperature, especially in winter when the temperature is low. Indoor natural maintenance in a short term can hardly meet the rapid strength growth of concrete. As a result, the processing efficiency of concrete products is low. To address this problem, an appropriate amount of early strength agent is widely used in the concrete to enhance its early strength. There are a large variety of concrete premature strength agent variety, which can be generally categorized into three groups: Inorganic salt premature strength agent, organic premature strength agent and compound premature strength agent[1]. Leng et al.[2] found that within the range of 0.5%—2%, chloride salt ($CaCl_2$, NaCl) increased the early strength of concrete with the increase of dosages. For example, the 3 d compressive strength increased by 30%—50% with the addition of chloride salt. However, chloride salt has a great impact on the setting process of cement. Moreover, the presence of chloride ions would cause the corrosion of reinforced steel. Thus, the combined use of compound nitrite is required[2-3]. Xie found that the 1 d strength of concrete mixed with triethanolamine increased by 6—9 MPa[4], but the optimal dosage of triethanolamine cannot be easily controlled. Therefore, a serious retardation in cement setting and a corresponding reduction in strength have been commonly observed. Wang et al.[5] showed that the 7 d compressive strength of mortar doped with calcium formate at room temperature was increased from 27.8—36.9 MPa at a dosage below 2.5%. However, at a higher calcium formate dosage, the specimens tended to set rapidly and produce cracks[5-6]. To et al.[7-8] used crystal species, high-valent cationic sulfate,

---

[*] Corresponding author, E-mail address: gengfei@nuaa.edu.cn.

How to cite this article: GENG Fei, LIANG Zizhao, YANG Hangli, et al. Effect of silica fume on early performance of precast concrete with early strength agents[J]. Transactions of Nanjing University of Aeronautics and Astronautics, 2022, 39(S): 90-97.

http://dx.doi.org/10.16356/j.1005-1120.2022.S.012

and hydrocarbon-based carboxylic acid compound to make a new type of early strength agent and found that the addition of the developed early strength agent in the concrete increased the 1 d, 3 d, and 7 d strength by approximately 100%, 70%, and 30%, respectively, with shortening the initial setting time and final setting time by 74 and 81 min, respectively[7-8]. From the above research, it can be seen that the early strength agent normally improves the early strength development of concrete. However, it is difficult to control the optimal dosage of the early strength agents, and their underlying early-strength enhancing mechanisms remain elusive. The early strength agent is effective at a relatively lower dosage. At excessive levels, however, the release of large amounts of hydration heat would cause cracking of the host materials.

Fly ash (FA) has been commonly used in practice to partially replace cement to lower the hydration heat at an early stage due to the slow pozzolanic reaction. At a curing age of 28 d, only about 2% of FA is reacted[9]. To circumvent this limitation, the combined use of highly reactive silica fume with FA has been attempted. Zhang et al.[10] found that replacing cement with 10% silica fume and the addition of 1.1% superplasticizer obtained the optimal proportion of high-performance concrete, which had a 28 d compressive strength of 92.7 MPa. Zhou et al.[11] reported that the swelling rate of mortars incorporated with 10% FA, 5% silica fume, and 0.04% air-entraining agent was only 0.08% after 24 h, which could also inhibit alkaline-silica-reaction (ASR). Li et al.[12] showed that at a curing temperature of -10 ℃, the 28 d compressive strength of concrete mixed with silica fume with a specific surface area of 18.2 m^2/g was increased by 35.9%. These studies demonstrated that the addition of an appropriate amount of highly active silica fume in the concrete can further improve the early age strength. However, less is known about the influencing degree of silica fume on the strength of concrete blended with early strength agent and the underlying mechanism remains unclear.

This study employed the ternary compounding technology of silica fume, FA, and early strength agent to investigate their effects on the early performance of concrete by monitoring changes in the compressive strength, hydration heat, hydration products, and microstructures. Through a comprehensive study, the most suitable amount of silica fume was determined, and its acting mechanisms were dissected.

1 Materials, Protocols, and Methods

1.1 Materials

The cement used in this study was P· Ⅱ 52.5 cement, and Grade Ⅱ fly ash produced by a thermal power plant was used. The fine aggregate was natural river sand with a dry state bulk density of 1 440 kg/m^3, and the coarse aggregate consisted of 5—16 mm melon flakes mixed with 5—25 mm coarse crushed in a certain proportion. PCA-9 with 8.8% solids, 1.022 g/cm^3 density, and 20% water reduction rate was used for the production of crystalline nucleated early strength agent (code for Z). The used silica fume (code for SF) had a apparent density of 1.30 g/cm^3 and a specific surface area of 22 300 m^2/kg. The chemical composition of SF is shown in Table 1. Tap water was used for all the tests.

Table 1 Chemical composition of silica fume %

Symbol	Loss on ignition	SiO_2	SO_3	CaO	MgO	Fe_2O_3	Al_2O_3	K_2O	Na_2O
W	5.32	90.75	0.98	0.09	0.40	0.21	0.48	0.54	0.24

1.2 Protocols

C30 concrete was selected due to its wide application in precast concrete. The amount of cementitious material was fixed at 4% with the addition of varying contents of SF (3%, 6%, and 9% (weight percent) of cementitious material). The mixing proportion of the precast concrete is shown in Table 2. The early strength performance of specimens with dimensions of 100 mm × 100 mm × 100 mm was investigated by measuring and comparing the compressive strength at 12 h, 14 h, 16 h, 1 d, and 3 d under natural curing (at ambient temperature of 20 ℃). The specimens were demoulded after 30 min at the test age. The optimum dosage of SF was determined based on the results of the early strength test. Moreover, the hydration heat of the cementitious slurry with the optimum content of SF was tested. Also, the hydration products, microscopic morphology, and pore structures of the 1 d and 3 d cured specimens were analyzed.

Table 2 Concrete proportion for testing kg/m^3

Symbol	C	FA	SF	S	G	W	PCA-9	Z
Z4%	272	68	0	792	1 054	154.4	4.76	13.6
Z4%+SF3%		57.8	10.2					
Z4%+SF6%		47.6	20.4					
Z4%+SF9%		37.4	30.6					

1.3 Methods

The compressive strength of concrete was tested in accordance with GB/T 50081—2019. The heat of hydration was measured according to the direct measurement method of GB/T 12959—2008. Cement hydration products were analyzed using qualitative X-ray diffraction (QXRD) analysis. The microscopic morphology of the early-strengthening-agent-doped concrete was examined by scanning electron microscopy (SEM). The pore structures of the early-strengthening agent-doped concrete were examined using the mercury-in-pressure (MIP) method.

2 Results and Discussion

2.1 Effect of silica fume on the early strength

The initial compressive strength test results of the concrete are shown in Figs.1, 2.

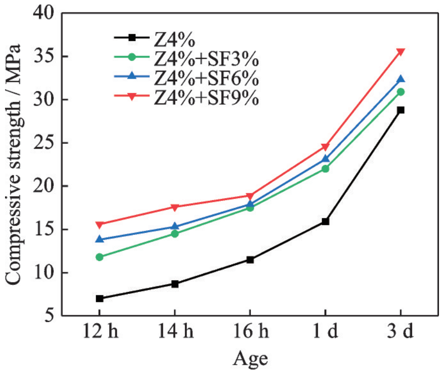


Fig.1 Compressive strength of concrete

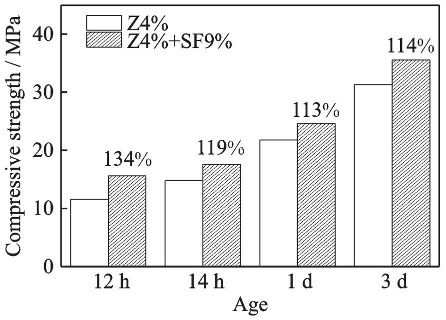


Fig.2 Compressive strength ratio of concrete

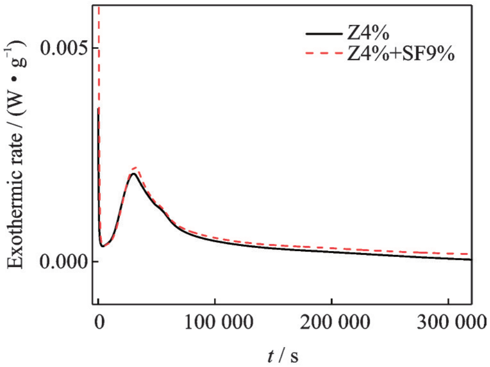
JGJ 1—2014 stipulates that the cubic compressive strength of the precast concrete should meet the design requirements and should not be less than 15 MPa when the precast is removed from the mould to prevent premature deformation or cracking. As seen in Figs.1, 2, the concrete mixed with 4% early strength agent reached a compressive strength of 18.5 MPa at 16 h, indicating that the specimens could be demoulded within 16 h. The compressive strength of concrete mixed with early strength agent and 3% SF was not significantly increased compared to that of concrete mixed with early strength agent alone. Instead, it was slightly lower than that of concrete mixed with early strength agent alone at 14 h, 16 h, and 3 d. When the SF content was increased to 6%, the compressive strength of the concrete was correspondingly increased and was more stable, which was only slightly lower than that of the concrete with the early strength agent alone at 16 h. When the SF content reached 9%, the compressive strength of the early strength agent doped concrete was improved more obviously, reaching 15.6 MPa at 12 h with its compressive strength ratio reaching 134%.

In summary, SF generally had a boosting effect on the early strength of the early strength agents incorporated concrete. For example, the addition of 9% SF in C30 concrete significantly promoted the cement setting and hardening at 12 h with a corresponding improvement in the early strength. Under natural curing conditions (with an average temperature of not less than 20 ℃), the compressive strength of the 9% SF incorporated concrete exceeded the requirements of the de-molding strength within 12 h.

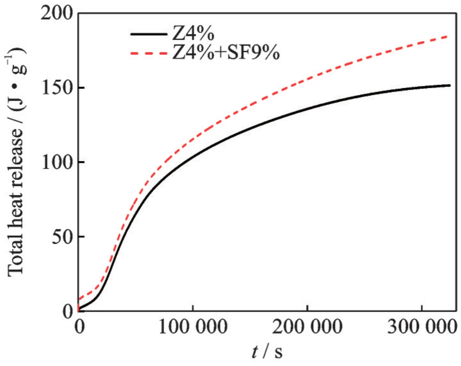
2.2 Effect of silica fume on the early hydration properties

2.2.1 Hydration heat of concrete

The hydration process of cement is accompanied by a series of exothermic reactions: The faster the exotherm of hydration, the faster its early hydration, and the higher its early strength. Based on the compressive strength test results, the 9% SF incorporated specimens were selected for the hydration heat test. The test results are shown in Fig.3.



(a) Exothermic rate of hydration



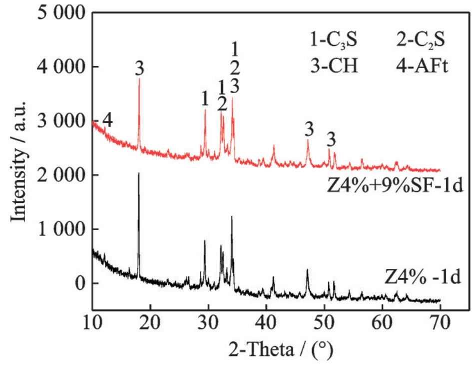
(b) Total exothermic hydration

Fig.3 Exothermic rate and heat release of cement-based materials

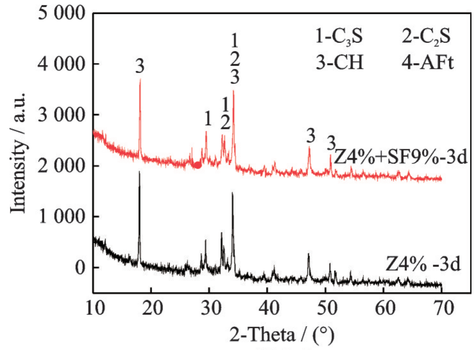
The hydration of cement is the driving force behind the hardening and strength development of the cementitious material. The easiest way to track the process of cement hydration is to monitor the change in heat during the hydration reaction. From a dynamic standpoint, the hydration of cementitious materials is normally measured in terms of two important parameters: The rate of the hydration reaction and the amount of heat released by the hydration reaction. The hydration process of cement can be generally divided into five stages: Initiation, induction, acceleration, deceleration, and stabilization[13]. Fig. 3 shows that the rates of exothermic hydration of the specimens with 9% SF and without SF were similar in the first four stages with only slight variations during the acceleration and deceleration periods: The heat releasing rate of the SF incorporated cementitious slurry was slightly higher than that of the non-SF cementitious slurry. During the stabilization period, both the heat releasing rate and total exothermic hydration of the 9% SF incorporated cement slurry mixed with the early-strengthening agent was substantially higher than that of its counterpart with the early-strengthening agent alone.

2.2.2 Concrete hydration products

To further investigate the effect of SF on the early hydration properties of the early strength agent doped concrete, XRD analysis was performed on the two sets of specimens. The XRD patterns of the two sets of specimens at 1 d and 3 d are shown in Fig.4.



(a) 1 d



(b) 3 d

Fig.4 XRD patterns of cement specimens

In Fig.4, SF had a negligible effect on the hydration products at the beginning of hydration, reflected by similar diffraction peaks of calcium hydroxide and early hydration products in the two sets of samples. This was attributed to the fact that the calcium hydroxide (CH) and hydrated calcium silicate (C-S-H) contents at the beginning of hydration were mainly influenced by the hydration degree of cement, which helped to explain why the hydration rate did not improve much in the first four stages, as shown in the hydration heat test. As cement continued to hydrate, the C-S-H and CH contents increased gradually. Meanwhile, SF gradually started to react with CH to form secondary C-S-H gels. As a result, the CH diffraction peak of the SF incorporated samples at 3 d started to decrease.

Overall, it could be seen that the hydration degree of cement in the early stages was mainly controlled by the water-to-cement ratio and cement particle size, and the influence of SF could be ignored. Initially, the cement particles in different systems showed a small difference in the free surface zone, and their contact area with water was similar. Thus, the difference in the initial hydration degree of cement was small. The main component of SF, SiO_2, was able to react with CH in the hydrated cement paste through the pozzolanic reaction to produce secondary C-S-H as the hydration reaction continued, Consequently, SF increased the hydration degree of the early strength agent incorporated cementitious materials[14-15].

2.3 Effect of silica fume on the early microstructure

2.3.1 Concrete microformat

The microstructures of the two groups of concrete were examined to further investigate the strength-enhancing mechanism of SF, and the results are shown in Figs.5, 6.

In Fig.5, after 1 d of cement hydration, the two sets of specimens produced calcium alumina, a large amount of gel materials, and hexagonal plates of CH with a large number of nanoscale particles distributed on the surface and a tightly lapped overall structure. Comparing the two groups of specimens, it can be seen that the surface of the SF doped specimen was distributed with a large number of unreacted particles, which filled in the fine pores of the hydration products, making the overall compactness of the cementitious material higher, which in turn enhanced the early strength.

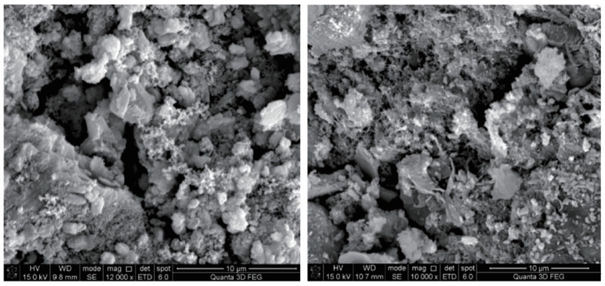

(a) Z4% (b) Z4%+SF9%

Fig.5 SEM images of concrete at 1 d

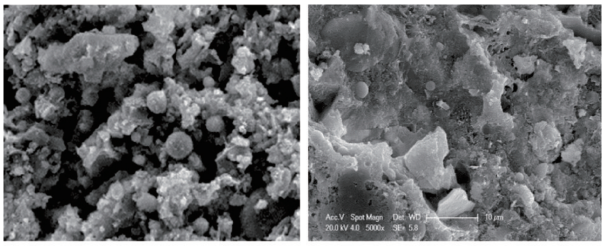

(a) Z4% (b) Z4%+SF9%

Fig.6 SEM images of concrete at 3 d

In Fig.6, with the evolution of cement hydration, the specimens in both groups generated larger ellipsoidal hydration products after 3 d. Other hydration products such as calcium alumina and CH were generated and accumulated more closely to each other. Comparing the two sets of specimens, it could be seen that SF filled the small pores between the cement particles, improved the particle gradation, and increased the compactness of the cementitious materials. The ellipsoidal hydration products, calcium alumina and CH on the surface of concrete mixed with both SF and early strength agent were fewer than those of concrete mixed with early strength agent alone. This was because the large specific surface area of SF provided more nucleation sites for the hydration products and thereby promoted cement hydration. Moreover, the pozzolanic reaction between SF and (CH generated more C-S-H, further improved the microstructures[14].

2.3.2 Concrete hole structure

For further investigate the effect of SF on the early microstructures of the early strength agent doped concrete, MIP analysis was performed on the two sets of specimens after standard curing for 1 d and 3 d. The results are shown in Table 3.

Table 3 Parameters characterizing the pore structure of concrete

Feature	1 d		3 d	
	Z4%	Z4%+SF9%	Z4%	Z4%+SF9%
Porosity/ %	18.60	21.60	18.90	18.00
Total pore volume/ $(\mathrm{ml{\cdot}g^{-1}})$	0.09	0.11	0.09	0.09
Specific surface area/ $(\mathrm{m^2{\cdot}g^{-1}})$	6.15	8.15	9.22	9.52
Most probable aperture/nm	7.51	7.11	7.11	7.14
Average pore diameter/nm	57.84	53.07	40.74	36.94

In Table 3, the porosity of the Z4%+SF9% specimen at 1 d was 21.6%, which was higher than that of the Z4% specimen, but its average pore size and most available pore size were 53.07 and 7.114 nm, respectively, both of which were lower than that of the Z4% specimen. This was due to the SF-induced particle filling effect that reduced some of the large pores in the concrete. Especially, the pozzolanic reaction of SF generated more secondary hydration products, which filled the pores in the concrete. As a result, the porosity of the Z4% and Z4%+SF9% specimens at 3 d was 18.9% and 18%, respectively. The pores in concrete could be generally divided into four categories: Harmless pores (pore size <20 nm), less harmful pores (pore size between 20 nm—50 nm), harmful pores (pore size >50 nm—200 nm), and more harmful pores (pore size >200 nm)[16]. The inclusion of SF in concrete reduced the average pore size to 36.94 nm at 3 d, which prevented the generation of harmful pores and more harmful pores, thereby improving the strength of concrete.

The incorporation of SF filled the fine pores between the cement particles, reduced the pore size, and thereby improved the compactness of the cementitious material. Moreover, the large specific surface area of SF could also provide more nucleation sites for the hydration products, which would induce a promoting effect on cement hydration. In addition, the higher pozzolanic reactivity of SF could produce more secondary C-S-H via reacting with CH derived from cement hydration to further improve the microstructures of cementitious materials, which was translated into an improved early strength.

3 Conclusions

Highly reactive silica fume improves the early performance of the precast concrete mixed with early strength agents. However, the influencing factors remain elusive. This study combines macroscopic and microscopic experimental analysis to determine the optimum dosage of silica fume and dissect the underlying mechanisms of silica fume in improving the early performance of the early-strengthening agent-doped concrete. Based on the findings from this study, the following conclusions can be drawn:

(1) When the silica fume content reached 9%, the compressive strength of C30 concrete mixed with the early strength agent was significantly improved. Under natural curing conditions (with an average temperature of not less than 20 ℃), the compressive strength of the 9% silica fume incorpoated concrete exceeded the requirement of the demoulding strength within 12 h.

(2) The difference in the hydration degree of cement at the beginning was small, which was mainly influenced by the water-to-cement ratio and cement particle size, and the difference in the free surface area of the cement particles in different systems at the beginning of hydration was also limited. Thus, the contact area with water was similar. After the cement hydration reaction, silica fume had a pozzolanic reaction, which increased the hydration degree and hydration rate of the early strength agent incorporated cementitious materials.

(3) Silica fume filled the fine pores between the cement particles, providing more nucleation

sites for the hydration products and thereby improving the pore size. Moreover, the pozzolanic reaction induced by silica fume generated more secondary CSH, which further improved the microstructures of the cementitious material and thereby increased the early strength of concrete mixed with the early strength agent.

References

[1] JIANG M F, LV X J. Research and application progress of concrete early strength agent[J]. Silicate Bulletin, 2014, 33(10): 2527-2533.

[2] LENG D, ZHANG X, SHEN Z L. Effect of water reducing agent and early strength agent on the performance of cement-based grouting materials[J]. New Building Materials, 2008(11): 21-25.

[3] ZHANG C. Compounding of cement-based grouting materials with early strength agents[J]. Science and Technology Wind, 2010(22): 156-157.

[4] XIE X J. Research on the application technology of concrete early strength agent[J]. New Building Materials, 2005(5): 33-35.

[5] WANG J, SONG D, WU T W. Analysis of the effect and mechanism of calcium formate in different polymeric waterproofing mortar systems[J]. China Construction Waterproofing, 2013(8): 23-26.

[6] XU F T, CHEN R, GU K. Application of calcium formate early strength agent in a dry mortar[J]. Wall Material Innovation and Building Energy Efficiency, 2008(2): 56-58.

[7] TO B W, DING Q J, MEI S G, et al. Research on the effect of new early strength agents on the performance of concrete[J]. Concrete, 2005(9): 49-54.

[8] TO B W, WANG Y P, WANG Q H, et al. Research on new early strength agents for concrete with low chlorine and low alkali[J]. Concrete and Cement Products, 2006(3): 1-4.

[9] YAN P Y. Mechanism of the role of fly ash in the hydration process of composite cementitious materials[J]. Journal of Silicate, 2007(S1): 167-171.

[10] ZHANG X X, YANG S L, DIAO B, et al. Effect of silica fume and superplasticizer admixture on the strength and fluidity of high-performance concrete[J]. Journal of Building Structures, 2009, 30(S2): 324-327.

[11] ZHOU S G, HE T S. Study on the effect of mineral admixtures and admixtures on the inhibition of ASR[J]. Journal of Xi'an University of Architecture and Technology (Natural Science Edition), 2010, 42(1): 137-141.

[12] LI Y, LIU R Q, QI W H, et al. Effect of silica fume particle size distribution on the microstructure of concrete and its low-temperature compressive strength[J]. China Powder Technology, 2019, 25(6): 75-80.

[13] LI Y. Study on low-temperature hydration characteristics of silicate cement-silica fume composite cementitious materials[D]. Dalian, China: Dalian University of Technology, 2016.

[14] ZHAO W. Simulation study on the effect of silica fume on the hydration and microstructure of cementitious materials[D]. Changsha, China: Hunan University, 2019.

[15] YE D Z. Study on the effect of silica fume on the performance of cement net paste and mortar and mortar structure[J]. Journal of Beijing University of Technology and Business (Natural Science Edition), 2007(6): 11-15.

[16] HE B. Effect of fly ash on the pore structure of low-temperature concrete[D]. Shenyang, China: Shenyang University of Architecture, 2016.

Acknowledgement This paper was supported by the 2020 Taizhou Science and Technology SME Incubation Programme.

Author Dr. **Geng Fei** received his B.S. and M.S. degrees in materials science and engineering from Southeast University in 2001 and 2004, respectively, and his Ph.D. degree in road and railway engineering from Nanjing University of Aeronautics and Astronautics in 2013. He is currently an associate professor in college of Civil Aviation at Nanjing University of Aeronautics and Astronautics, where his main research interests are in high-performance/functional cement-based materials and structures, and pavement paving materials and structures.

Author contributions Dr. **GENG Fei** presented the innovative points and first draft ideas of the article. Mr. **LIANG Zizhao** conducted the experimental design and main data analysis. Ms. **YANG Hangli** carried out the revision and finalization of the paper writing. Mr. **WU Zhongqin** provided references for the experimental design. Mr. **ZHU Xiongwei** provided reference advice on the writing of the manuscript. Mr. **XU Junlun** participated in some of the data analysis. All authors commented on the manuscript draft and approved the submission.

Competing interests The authors declare no competing interests.

(Production Editor: ZHANG Bei)

硅灰对掺早强剂预制构件混凝土早期性能的影响

耿 飞[1]，梁子朝[1]，杨杭莉[1]，吴仲勤[2]，朱雄威[2]，许峻伦[1]

（1.南京航空航天大学民航学院，南京 211106，中国；2.江苏宇辉住宅工业有限公司，泰州 225300，中国）

摘要：为研究硅灰对掺早强剂预制构件混凝土早期性能影响，采用硅灰、粉煤灰和早强剂三元复掺技术，测试分析混凝土抗压强度、水化热、水化产物及微观结构，探究硅灰对掺早强剂预制混凝土构件早期性能影响。试验结果表明：掺早强剂预制混凝土构件中硅灰最适宜量为9%；硅灰填充了水泥颗粒间的细小孔隙，但水泥水化初期主要受水胶比及水泥粒径影响；随着水化反应的不断进行，硅灰提供更多成核表面，特有的火山灰反应使掺早强剂水泥基材料水化程度及水化速率增大。

关键词：硅灰；混凝土；早期强度；水化热；孔结构