Study on the early performance of silica fume-slag inorganic polymer

Hengbo Zhang 1, Jinyu Xu 2,3, Xin Luo 1*, Huang Yu 1 and Liangxue Nie 4

1 National Defense Engineering Institute, Academy of Military Sciences, Beijing, 100036, China
2 Teaching-research Office of Airfield and Building Engineering, Air Force Engineering University, Xi’an, Shanxi 710038, China
3 College of Mechanics and Civil Architecture, Northwest Polytechnical University, Xi’an, Shanxi, 710072, China
4 93125 troops of PLA, Xuzhou, Jiangsu, 221005, China
*Corresponding author’s e-mail: luoxin_01@163.com

Abstract. Based on the slag inorganic polymer, the silica fume-slag inorganic polymer (SSIP) with the ordinary and semi-dense silica fume slag content of 5%, 10%, 15%, 20%, 25 and 30%, respectively, were prepared, the working performances, early mechanical properties and the phase of SSIP were studied. The results show that: two kinds of silica fume both can prolong the initial and final setting time of SSIP to a certain extent and improve the working performance, but on the whole, the addition of silica fumes will weaken the compressive and flexural strength, thus reduce the early mechanical properties; The XRD spectrum of SSIP has no obvious change after adding silica fumes, the phase composition of two kinds of SSIP was similar, and the larger the silica fume content is, the higher the amorphous content of SSIP is.

1. Introduction

Cement concrete is the most dependent building material at present, its stable working performance, excellent durability, low economic cost and simple preparation process make it still occupy an unshakable position in the era of rapid development of material science. But for the construction field with special requirements, such as emergency repair and construction projects, traditional concrete cannot meet the actual needs.

With the development of cement materials, there have been many kinds of high-efficiency fast hardening cement, such as quick setting and hardening cement [1, 2], fast hardening sulfoaluminate cement [3, 4], magnesium cement [5, 6], magnesium phosphate cement [7, 8] and potassium magnesium phosphate cement [9-11], etc. have coming into use one after another. The fast hardening sulfoaluminate cement concrete can be demoulded smoothly in 4~5 h, and its strength can exceed 30~40 MPa in 12 h [4]; the magnesium phosphate cement concrete can be demoulded after casting for 1 h, and the strength can be more than 30 MPa in 6 h [8]. Although these high-efficiency cements have the properties of excellent quick hardening and early strength, their economic cost and preparation difficulty are relatively high, which is the main reason for limiting their widely use. Therefore, it is imperative to find a new type of building material with low price, stable property and excellent performance, and the early strength inorganic polymer materials came into being.
Slag is a by-product in the process of blast furnace ironmaking, its physical and chemical properties are highly stable, and it is the common raw material of inorganic polymer materials at present. However, some studies have shown that [12-14], the alkali activation of slag is very active, under the action of alkali activator, the setting time of slag is extremely short, which is not conducive to the actual construction and brings great difficulty to the emergency repair and construction work. In view of this, referring to the current research results, based on the slag based early strength inorganic polymer, silica fume-slag inorganic polymer (SSIP) with the ordinary and semi-dense silica fume slag content of 5%, 10%, 15%, 20%, 25 and 30% respectively, were prepared by the method of internal mixing, the working performance and early mechanical properties were studied, and the phase composition was further analyzed by X-ray diffractometer (XRD).

2. Experiment

2.1. Raw materials

The raw materials of inorganic polymer mainly include solid-phase materials and alkali activator. Slag is selected as the solid-phase material, and the main performance indexes are shown in Table 1, the solid-phase material is also called the precursor for preparing inorganic polymer; alkali activator is prepared by water, sodium silicate and flake alkali; tap water; the modulus of sodium silicate is 3.2~3.4, the mass fraction is about 34%, and the density is about 1370 kg/m³; the main component of flake alkali is NaOH with the purity of 99%.

Table 1. Performance indexes of slag

| Density (g/cm³) | Specific surface area (m²/kg) | Loss on ignition (%) | Moisture content (%) | Fluidity ratio (%) | 7-day activity index (%) | 28-day activity index (%) |
|----------------|-------------------------------|----------------------|----------------------|-------------------|-------------------------|-------------------------|
| 2.89           | 478                           | 0.6                  | 0.3                  | 101               | 89                      | 105                     |

The preparation of SSIP is to replace part of slag by silica fume, and the silica fume content are 5%, 10%, 15%, 20%, 25 and 30% of the total mass of solid-phase cementitious materials respectively. Two types of silica fume, ordinary and semi-dense silica fume (the main performance indexes are shown in Table 2), are used to prepare SSIP, which are marked as SSIP1 and SSIP2.

Table 2. Parameters of silica fume

| Silica fume type | Density (kg/m³) | Loss on ignition (%) | Moisture content (%) | Alkali content (%) | Silica content (%) |
|------------------|-----------------|----------------------|----------------------|-------------------|-------------------|
| Ordinary         | 200             | 2.7                  | 0.04                 | 0.54              | 98.2              |
| Semi-dense       | 350             | 2.7                  | 0.04                 | 0.54              | 98.2              |

2.2. Experiment scheme

The raw material mix of 1 kg slag inorganic polymer is shown in Table 3, the preparation of SSIP is based on this basic mix proportion, and according to the method of internal mixing, the slag is replaced by the same mass of silica fume.

Table 3. Mix proportions of 1 kg slag inorganic polymer (kg)

| Slag | Water | Sodium silicate | Flake alkali |
|------|-------|-----------------|--------------|
| 0.645| 0.101 | 0.204           | 0.050        |

During the preparation of SSIP, the silica fume and slag should be mixed evenly in advance to prepare the precursor, the mixer is started to premix at low speed for 30 s, and then the prepared alkali activator is added uniformly. Because of the corrosiveness of alkali activator, proper protective measures should be taken when adding the alkali activator, after adding the solution, the mixture should be mixed slowly for 30 s and then quickly for 30 s.

Pour the mixture into the Vicat apparatus, the performance test includes the working performances (setting time, fluidity) and early mechanical properties (compressive and flexural strength at the age of 1 h, 2 h and 3 h). The initial setting and final setting time of the mixture are tested according to the
national standard of test method for water requirement of normal consistency, setting time and soundness of portland cement (GB/T 1346-2011, in Chinese), the fluidity test is carried out according to the jumping table method in the national standard of test method for fluidity of cement mortar (GB/T 2419-2005, in Chinese), and the strength experiment is conducted according to the of method of testing cements-Determination of strength (GB/T 17671-1999, in Chinese).

It is important to note that, the casted specimens should be placed for 1 h, and after demoulded they are moved into the curing room for standard maintenance with the condition of temperature maintains in 20±2 °C and relative humidity doesn’t less than 95%. According to the requirements of standards, the size of SSIP specimens for compressive and flexural strength test is 40 mm×40 mm×160 mm.

3. Experiment results

3.1. Analysis of working performances

The working performances of SSIP1 and SSIP2 specimens are shown in Figure 1 (setting time) and Figure 2 (fluidity).

![Figure 1. Setting time](image1)

![Figure 2. Fluidity](image2)

The initial setting time $T_i$ is slightly longer due to the addition of ordinary silica fume, and the $T_i$ has a small change magnitude with the increase of silica fume content. The addition of semi-dense silica fume has a positive correlation with the $T_i$, and when the addition content is 30%, the $T_i$ reaches 22 min, which is 100% higher than that when the addition is 0%.

The final setting time $T_f$ has no obvious change after adding ordinary silica fume, while the addition of semi-dense silica fume also has a positive correlation with the $T_f$, and the $T_f$ reaches 41 min with 30% addition, which is 95.2% higher than that when the addition is 0%.

There is a significant negative correlation between the content of silica fume and the fluidity, the lowest fluidity is 98 mm when the content is 30%, which is 45.9% lower than that when the content is 0%. With the increase of the semi-dense silica fume, the fluidity first increases and then decreases, the fluidity can reach 215 mm at most, which is 18.8% higher than that when there is no silica fume added. When the content is higher than 15%, the fluidity begins to decrease, and the minimum fluidity is only 131 mm, which is 27.6% lower than that the content is 0%.

Silica fume is a kind of micron powder material, the average particle size is 0.1~0.3 μm, and the particle size less than 1 μm accounts for more than 80%. According to the properties of the materials, the finer the particles, the larger the specific surface area is, and the higher the activity is, therefore, the addition of silica fume can make the polymerization of the material more thorough, that is, the reaction takes longer, the $T_i$ and $T_f$ are gradually extended with the increase of silica fume content at the macro level. The activity of powder also has a significant effect on the fluidity of materials, the higher the activity, the greater the fluidity.

3.2. Analysis of early mechanical properties

The early compressive strength and flexural strength of SSIP1 and SSIP2 specimens are shown in Figure 3 and Figure 4 respectively.
The compressive strength $f_c$ of SSIP1 and SSIP2 decreased with the increase of silica fume content at each age, the $f_c$ of SSIP1 decreased by 86.1%, 78.8% and 74.9% at the age of 1 h, 2 h and 3 h as the content of ordinary silica fume is 30% when compared with no silica fume addition, while the $f_c$ of SSIP2 have the decrease of 55.2%, 64.1% and 32.9%. The $f_c$ of SSIP2 is generally higher or close to that of SSIP1 at the same silica fume content, that is to say, the deterioration to $f_c$ of ordinary silica fume is more serious than that of semi-dense silica fume.

There is a negative correlation between the content of two kinds of silica fume and the flexural strength $f_f$, the higher the content of silica fume, the more the strength will decrease. It should be noted that the $f_f$ at the age of 3 h can be improved by adding low content of semi-dense silica fume, when the content is 5% and 10%, the $f_f$ are increased by 23.2% and 9.87%, and the $f_c$ of SSIP2 is 40 MPa and 37.3 MPa respectively at this time, the decrease is very small when compared with the 41.9 MPa of no silica fume addition.

The formation of strength is mainly occurs in the early stage of the reaction, during which a large number of C-S-H has been formed, and the C-S-H is the main source of early strength of inorganic polymer [15]. In addition, there are also polymerization products of silicon oxygen tetrahedron and aluminum tetrahedron, which will react with alkali metals to form oligomeric polymer, and constantly change to high polymer, and forming a relatively stable three-dimensional network structure. In a certain addition range, the higher the slag content, the more C-S-H and three-dimensional network structure will be generated, thus the higher the strength, but the polymerization of silica fume does not have this effect. Furthermore, the early polymerization of slag is often accompanied by "three highs" (the concentration of calcium ion and silicon oxygen ion is very high, the pH of the solution is very high, and the hydration heat makes the temperature of the solution very high), this phenomenon will accelerate the reaction process and promote the degree of reaction. For these reasons, after adding silica fume, the content of slag powder is relatively reduced, the early strength of inorganic polymer will be weakened, and the higher the content of silica fume, the more serious the strength loss.

In conclusion, it is considered that the low content (5%~15%) of semi-dense silica fume can improve the overall performance of SSIP, and the two kinds of silica fume with high content have no obvious enhancement effect on properties of SSIP in all aspects, and even produce degradation effect.

4. Analysis of phase composition

The phase analysis of SSIP was further carried out by XRD, before the test, the material was milled into powder, and the range of $2\theta$ was set as 10°~80°. The specimens include the control group with no silica fume addition and the test groups with the semi-dense silica fume content of 5% and 15%, which are corresponding to X, Y1 and Y2 in Figure 5 respectively. Since the phase composition of SSIP1 and SSIP2 is basically the same, the SSIP1 specimens will not be tested.
The result shows that the XRD spectrum of SSIP does not change obviously after adding silica fume, and the phase composition of specimens in each group are relatively close, the amorphous bodies account for a high proportion of materials. If the crystal is the region with obvious wave peak, and the amorphous is the region with halo peak or no obvious wave peak, according to the integral calculation of the corresponding area of the two regions, the ratio of crystal and amorphous in X is 32:68, the ratio of Y1 and Y2 are 39:61 and 48:52 respectively, which indicates that the larger the content of silica fume is, the higher the content of amorphous is.

Amorphous is the main part of the material, some small peaks are difficult to identify accurately, and there are four types of crystal components that can be determined in figure 11: calcium carbonate corresponds to the main peaks of 29° and 31°, calcium magnesium silicate corresponds to the main peaks of 33°, and calcium carbonate is the crystal with the largest content, followed by calcium magnesium silicate; the other two kinds of wave peaks with high identification, namely, mullite corresponds to the main peaks of 16° and 26°, quartz corresponds to the main peaks of 25°, and the larger the content of silica fume is, the higher the content of mullite and quartz crystal is.

5. Conclusions
In this paper, the working properties and early mechanical properties of two kinds of SSIP with the ordinary and semi-dense silica fume slag content of 5%, 10%, 15%, 20%, 25 and 30% are discussed, and the phase composition is further analyzed. The main conclusions are as follows:

(1) The $T_i$ is slightly longer with the addition of ordinary silica fume, the change magnitude is very small, and the $T_f$ has no obvious change; the content of semi-dense silica fume has positive correlation with $T_i$ and $T_f$, and when the content of semi-dense silica fume is 30%, the $T_i$ and $T_f$ are 22 min and 41 min respectively, which are 100% and 95.2% higher than that of no silica fume addition.

(2) There is a significant negative correlation between the content of silica fume and the fluidity, when the content is 30%, the lowest fluidity is 98 mm, which is 45.9% lower than that the content is 0%; with the increase of semi-dense silica fume, the fluidity first increases and then decreases, the fluidity can reach 215 mm at most when the content is 15%, which is 18.8% higher than that when there is no silica fume added.
(3) On the whole, the $f_c$ and $f_f$ of SSIP decrease with the increase of silica fume, when the content of semi-dense silica fume is 5% and 10%, the $f_f$ are increased by 23.2% and 9.87%, and the $f_c$ of SSIP2 is 40 MPa and 37.3 MPa respectively at this time, the decrease is very small when compared with the 41.9 MPa of no silica fume addition.

(4) XRD spectrum of SSIP does not change obviously after silica fume added, phase composition of specimens in each group are relatively close, and the crystal components that can be determined are calcium carbonate, calcium magnesium silicate, mullite and quartz; the proportion of amorphous in SSIP is very high, and the larger the content of silica fume is, the higher the content of amorphous is.

Acknowledgement
This work was sponsored by the key project of Military Scientific Research (JK20191A010001).

References
[1] Yu J, Yu G J. 2018. Underwater Non-Dispersible Quick-Setting and Rapid-Hardening Cement-Based Composite Material and Preparation Method and Application Therewith: U.S. Patent Application 15/946, 806 [P]. 2018-10-11.
[2] Li N, Shi C, Zhang Z. 2019. Understanding the roles of activators towards setting and hardening control of alkali-activated slag cement [J]. Composites Part B: Engineering, 171: 34-45.
[3] Zhang G, Li G, He T. 2017. Effects of sulfoaluminate cement on the strength and water stability of magnesium potassium phosphate cement [J]. Construction and Building Materials, 132: 335-342.
[4] Gong C, Zhou X, Dai W, et al. 2018. Effects of carbamide on fluidity and setting time of sulfoaluminate cement and properties of planting concrete from sulfoaluminate cement [J]. Construction & Building Materials, 182: 290-297.
[5] He P, Chi S, Daniel C. 2018. Comparison of glass powder and pulverized fuel ash for improving the water resistance of magnesium oxychloride cement [J]. Cement and Concrete Composites, 86: 98-109.
[6] Xu B, Ma H, Hu C, et al. 2016. Influence of cenospheres on properties of magnesium oxychloride cement-based composites [J]. Materials and Structures, 49(4): 1319-1326.
[7] Lahalle H, Coumes C C D, Mesbah A, et al. 2016. Investigation of magnesium phosphate cement hydration in diluted suspension and its retardation by boric acid[J]. Cement and Concrete Research, 87: 77-86.
[8] Feng H, Chen G, Gao D. 2018. Mechanical Properties of Steel Fiber-Reinforced Magnesium Phosphate Cement Mortar [J]. Advances in Civil Engineering, 3: 1-11.
[9] Ma C, Chen B. 2016. Properties of magnesium phosphate cement containing redispersible polymer powder [J]. Construction and Building Materials, 113: 255-263.
[10] Yu C, Wu Q, Yang J. 2017. Effect of seawater for mixing on properties of potassium magnesium phosphate cement paste [J]. Construction and Building Materials, 155: 217-227.
[11] Le Rouzic M, Chaussadent T, Platret G, et al. 2017. Mechanisms of k-struvite formation in magnesium phosphate cements [J]. Cement and Concrete Research, 91: 117-122.
[12] Onisei S, Pontikes Y, Van Gerven T, et al. 2012. Synthesis of inorganic polymers using fly ash and primary lead slag [J]. Journal of hazardous materials, 205: 101-110.
[13] Pontikes Y, Machiels L, Onisei S, et al. 2013. Slags with a high Al and Fe content as precursors for inorganic polymers [J]. Applied clay science, 73: 93-102.
[14] Giels M, Iacobescu R I, Cappuyns V, et al. 2019. Understanding the leaching behavior of inorganic polymers made of iron rich slags [J]. Journal of Cleaner Production, 238: 117736.
[15] Bernal S A, Gutiérrez R M D, Pedraza A L, et al. 2011. Effect of Binder Content on the Performance of Alkali-Activated Slag Concretes [J]. *Cement and Concrete Research*, 41: 1-8.