Effect of polycarboxylate superplasticizer on fluidity and rheology of cement slurry containing silica fume

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Abstract. The effect of polycarboxylate superplasticizer on the fluidity and rheology of cement - silica fume - water paste was investigated. The changes of dispersion degree, yield stress and plastic viscosity of paste with different superplasticizer content were analyzed. The results show that the rheological properties of paste with different superplasticizer content conform to Herschel-Bulkley model. The shear thinning of the slurry is manifested as a typical yielding pseudoplastic fluid characteristic. When the content of superplasticizer is less than 1.0%, the plastic viscosity and yield stress decrease and the fluidity increase with the increase of plasticizer content. When the content of superplasticizer is more than 1.0%, the yield stress decreases slightly and the plastic viscosity increases with the increase of plasticizer content. The fluidity decreases with the increase of yield stress, and there is a good correlation between them.

1 Introduction

High cement content, low water binder ratio and the use of silica fume(SF) give RPC a very dense microstructure. The inherent defects of RPC are greatly reduced, so it has ultra-high strength[1]. However, with the decrease of water binder ratio, the viscosity of cement paste gradually increases, causing a series of construction problems such as difficult mixing and pumping, which greatly limits its application[2]. The ball effect, activity effect and micro-aggregate filling effect of silica fume are used to optimize the rheological properties of cement paste, and the macro defect free structure of cement matrix is formed. However, the existence of ultrafine silica fume aggravates the formation of flocculated structure in the slurry. Polycarboxylate superplasticizer has strong electrostatic repulsion force and steric repulsion force[3], which can not only disperse flocculation structure, but also form hydration film on the surface of silica fume and cement to reduce the friction between particles.

The dispersion of polycarboxylate superplasticizer in cement- silica fume- water system was investigated. The influence of polycarboxylate superplasticizer on the dispersion degree, yield stress and plastic viscosity of cement-silica fume-water slurry was determined, and the influence law of its content on the fluidity and rheology of cement-silica fume-water system was grasped.

2 Experimental

2.1 Materials

Polycarboxylate superplasticizer, solid content of 40%, water reduction rate of 35%, Guangdong Hualixin Building Materials Technology Co., Ltd. Portland cement, P.I 42.5, Fushun Cement Co., Ltd. Silica fume, silica dioxide content of 93%, particle size of 0.1-1.0μm, density of 2.21g/cm³, specific surface area 2.0 × 10⁴m²/kg, Guangdong Qinshi new energy Co., Ltd. (Fig. 1).

Fig1. Morphology of silica fume

2.2 Mix design

In order to grasp the influence of polycarboxylate superplasticizer on the fluidity and rheology of cement paste containing silica fume, six mix proportions with different superplasticizer agent contents were prepared by keeping the silica fume content and water binder ratio unchanged. The content of silica fume is 25% and the water binder ratio is 0.19. The mix proportions are given

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in Table 1.

| Samples | Content of superplasticizer r/％ | Mix proportion / g | Cem | Silica fume | Water | Superplasticizer |
|---------|---------------------------------|-------------------|-----|------------|-------|-----------------|
| M3-1    | 0.4                             | 750               | 250 | 190        | 4     |                 |
| M3-2    | 0.6                             | 750               | 250 | 190        | 6     |                 |
| M3-3    | 0.8                             | 750               | 250 | 190        | 8     |                 |
| M3-4    | 1.0                             | 750               | 250 | 190        | 10    |                 |
| M3-5    | 1.2                             | 750               | 250 | 190        | 12    |                 |
| M3-6    | 1.6                             | 750               | 250 | 190        | 16    |                 |

2.3 Test methods

The fluidity test is carried out according to GB/T 8077-2012. The paste was poured into a slump cone. The cone was lifted up and the spread diameter of paste was recorded as the average of two perpendicularly crossing diameters at the set time. The rheological properties of paste were measured by a model RST-CC rheometer (Brookfield Co. Ltd., USA). In order to obtain the same shear state of each paste before rheological test, the test is divided into two stages: pre-shearing and data collection. The rheological mechanism is given in Fig. 2.

![Fig2. The rheological mechanism](image)

3 Results and discussion

3.1 Fluidity

When the water-to-binder ratio is very low, the tiny particles will wrap water to form a flocculation structure, an there is little free water in the paste. The superplasticizer adsorbed on the surface of the particles produced electrostatic repulsion to disperse the particles and release the water wrapped in the flocculation structure. At the same time, the adsorption layer has a strong steric hindrance, which reduces the friction between particles. The combined effect improves the fluidity of the mixture[4]. Figure 3 exhibits the dispersion-time curve of cement-silica fume-water paste with different superplasticizer content. When the content of superplasticizer is small, the fluidity increases with the increase of superplasticizer content. When the content of superplasticizer increased from 0.4% to 1.0%, the dispersion degree of paste in 150s increased from 84 mm to 159 mm, and the growth rate reached 89.3%. This is due to with the increase of the superplasticizer content, the flocculation structure was destroyed, the water was released, and the fluidity of paste increased. When the content of superplasticizer is more than 1.0%, the fluidity would not be improved, but slightly decreased. This is due to excessive additives increase the viscosity of the paste, resulting in the decline of fluidity.

![Fig3. Fluidity of cement-silica fume-water paste with different superplasticizer content](image)

3.2 Rheology

3.2.1 Rheological curve

The rheological curve can better reflect the influence of superplasticizer on the cement-silica fume-water paste. The paste exhibited shear thinning in the rheological experiment. The downward section of the rheological curve is located below the upward section to form a hysteresis loop (Figure 4). This is due to the failure of internal microstructure in the shear process, which leads to the decrease of shear stress when the shear rate is constant[5].

![Fig4. Hysteresis loop](image)
The rheological curve of cement-silica fume-water paste with a superplasticizer content of 0.4% to 1.6%. The rheological curve of paste with 0.4% superplasticizer is different from other samples. This is because when the content of superplasticizer is small, there are a lot of flocculation structure in the paste, free water is less, the distance between particles is close, and the shear resistance is correspondingly very large.

3.2.2 Rheological model

Table 2. Fitting results of rheological parameters

| Sample  | Content of superplasticizer/% | \( \tau_0 \)/Pa | \( \eta \)/Pa·s\(^n\) | n | R\(^2\) |
|---------|-------------------------------|----------------|----------------|---|------|
| M3-1    | 0.4                           | 99.46          | 55.28          | 0.51 | 0.99447 |
| M3-2    | 0.6                           | 24.59          | 20.44          | 0.74 | 0.99986 |
| M3-3    | 0.8                           | 7.65           | 20.69          | 0.75 | 0.99959 |
| M3-4    | 1.0                           | 5.99           | 20.84          | 0.74 | 0.99961 |
| M3-5    | 1.2                           | 5.80           | 27.76          | 0.73 | 0.99951 |
| M3-6    | 1.6                           | 2.06           | 26.90          | 0.73 | 0.99992 |

Many scholars believe that the fresh cement-based composite can be regarded as a plastic fluid, which can be analyzed by Bingham fluid model [9-11]. There are also views that it is not feasible to analyze fresh mortar by Bingham model [12]. Fig. 4 presents that the rheological curves of cement-silica fume-water paste with different superplasticizer contents show typical yield pseudoplastic fluid characteristics, which are consistent with Herschel-Bulkley model. The equation \( \tau = \tau_0 + m(\dot{\gamma})^n \) based on Herschel-Bulkley model was used to fit the paste with each superplasticizer content. The fitting results of rheological parameters are shown in Table 2.

It exhibits that the correlation coefficients of each rheological curve fitted by Herschel-Bulkley model are greater than 0.99. It shows that Herschel-Bulkley model can be applied to cement-silica fume-water paste containing polycarboxylate superplasticizer very well.

3.2.3 Rheological parameters

Table 2 presents the rheological index (n) of pastes with different superplasticizer contents is less than 1.00. It presents that the paste is a pseudoplastic fluid with shear thinning. This is due to the flocculation structure in the paste is broken and more free water is released. The plastic viscosity cannot be obtained directly from Herschel-Bulkley model. Ferris and de Larrard gave the empirical formula of plastic viscosity \( \mu = \frac{3m}{n+2} \gamma_{max}^{n-1} \) through a large number of experimental studies, where \( \gamma_{max} \) is the maximum shear rate in the test. Figure 6 exhibits the effect of superplasticizer content on the plastic viscosity and yield stress.

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difficult to be directly applied in engineering.

The change of rheological parameters determines the change of fluidity. Figure 7 shows that the fluidity decreases with the increase of yield stress. When the content of superplasticizer is low, the yield stress and plastic viscosity are large, and the dispersion of paste stops quickly. With the increase of superplasticizer content, the flocculation structure in the paste decreases, the hydration film on the surface of particles becomes thicker, and the yield stress decreases greatly. Hence, the dispersion resistance of the paste decreases, the dispersion time becomes longer, and the dispersion degree increases greatly. When the content of superplasticizer exceeds 1.0%, the excess superplasticizer only slightly reduces the yield stress and increases the plastic viscosity, so the dispersion degree of the paste is no longer increased. Both yield stress and fluidity indicate the interaction between particles in the paste without high-speed shear failure. There is a good correlation between them. The correlation coefficient (R2) is 0.9686 (Fig. 7).

**Fig7. Effect of superplasticizer on plastic viscosity and fluidity of cement paste containing silica fume**

### 4 Conclusion

The effect of polycarboxylate superplasticizer on fluidity and rheology of cement slurry containing silica fume was investigated, and the following conclusions were drawn.

1. The rheological curves of cement-silica fume-water paste with different polycarboxylate superplasticizer content exhibit typical yield pseudoplastic fluid characteristics. The correlation coefficients fitted by Herschel-Bulkley model were all greater than 0.99. The pastes with different superplasticizer content all show shear thinning, and the rheological index (n) is all less than 1.00.

2. When the superplasticizer content is 0.4%, a large number of flocculation structures are formed in the cement paste. The fresh composite lacks free water and the slip resistance between particles is high. Accordingly, the yield stress and plastic viscosity are large, which makes the paste difficult to dispersed.

3. When the content of superplasticizer increased from 0.4% to 1.0%, more flocculation structures were destroyed. At the same time, the hydration film on the surface of particles becomes thicker, the steric hindrance increases, and the slip resistance between particles decreases. The plastic viscosity and yield stress decreased and the fluidity increased. On the one hand, the friction force between the flowing particles is reduced, on the other hand, the flocculation structure is constantly destroyed when the paste moves at high speed.

4. When the content of superplasticizer is more than 1.0%, too much superplasticizer increases the viscosity of the paste. The yield stress decreases slightly, but the plastic viscosity increases slightly with the increase of superplasticizer content.

5. Both yield stress and fluidity indicate the interaction between particles in the paste without high-speed shear failure. There is a good correlation between them. The fluidity decreases with the increase of yield stress, and there is a good correlation between them.

### References

1. C.G. Long, Y.J. Xie, P.M. Wang, Z.W. Jiang, J. Ceram Soc, 33, 4 (2005), (In Chinese)
2. V. Živica, Constr. Build. Mater, 23 (2009)
3. Y.Q. Jiang, Application basis of concrete admixtures (Chemical Industry Press, 2011), (In Chinese)
4. R.J. Flatt, Y.F. Houst, Cem Concr Res, 31 (2001)
5. M.L. Cao, L. Xu, C. Zhang, J. Ceram Soc, 44, 2 (2016), (In Chinese)
6. H.H.C. Wong, A. Kwan, W.W.S. Fung, Adv Cemt Res, 22, 1 (2010)
7. A.K.H. Kwan, W.W.S. Fung, Cem Concr Compos, 34, (2012)
8. H. Vikan, H. Justnes, Cem Concr Res, 37, (2007)
9. C. Hu, F. Larrard, Cem Concr Res, 26, 2 (1996)
10. T. Yen, C.W. Tang, C.S. Chang, K.H. Chen, Cem Concr Compos, 21, (1999)
11. J. Golaszewski, J. Szوابowski, Cem Concr Res, 34, (2004)
12. J.Z. Liu, W. Sun, Q.Q. Zhang, J.P. Liu, Concr Cem Prod, 1, (2014), (In Chinese)
13. D.P. Bentz, C.F. Ferraris, M.A. Galler, A.S. Hansen, J.M. Guynn, Cem Concr Res, 42, (2012)