論文 A Study on Effect of Superfine Powders on Fluidity of Cement Paste

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ABSTRACT: The paper presents the results of experimental study on the effect of superfine powders made from vitrescence, crystalline state and amorphous material on the fluidity of cement paste. The experimental results indicated that vitrescence powders have dispersing effect on cement pastes, whereas the crystalline and amorphous powders have only filling effect. The different properties of the powders are associated to their micromorpha. Especially, action machanism of vitrescence powder has been discussed.
KEYWORDS: superfine powder, vitrescence, crystalline, amorphous, dispersing effect, filling effect

1. INTRODUCTION

High performance concrete (HPC) has focused more attention on its advantages over ordinary concrete, which includes mainly good workability, high strength, and superior durability. In manufacturing HPC, superfine powders are usually used together with superplasticizer. Series of physical chemistry actions can be generated in the concrete by using the both materials simultaneously. The main role of this dosing method is the fluiding effect in the fresh concrete stage. In other words, the concrete containing superfine powder in combination with superplasticizer exhibits that prominent fluidity over the concrete with superplasticizer alone, through the filling effect and the dispersing effect of the powders. Many authors hold the view that the increment of HPC is attributed to the filling effect of the powders [3, 4, 5]. However, in this experimental study the dispersing effect of the powders is demonstrated for the first time, which is more significant to enhance the fluidity of HPC than the filling effect. The results of the experimental study would be of useful reference value in high performance concrete.

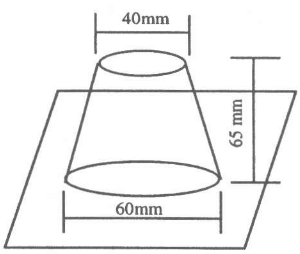

Fig.1 Apparatus for fluidity test

2. EXPERIMENTAL

2.1 EXPERIMENTAL METHODS

1) Chemical composition of the cement and the powders were clarified with chemical analysis.

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2) Phases of the powders were identified by using X-Ray Diffraction (XRD) method.

3) Fluidity of the pastes was examined through a flow spread test. In the experimental process, a frustum of cone was used to keep the paste (as shown in **Fig.1**). After filling with the paste, the cone was lifted and the paste spread naturally on the glass plate, then the average diameters were measured.

4) Viscosity of the pastes was measured with the rotational viscometer.

Table 1 Composition of cement and powders (%)

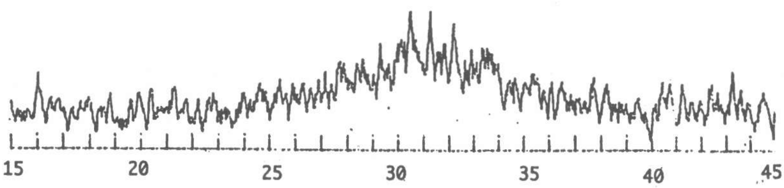
Composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3
Cement	64.50	22.30	4.30	3.50	2.60	2.30
BFS	37.51	33.20	12.60	4.60	7.63	0.24
PS	44.40	36.90	3.92	2.90	1.56	0.20
QS	2.06	75.93	10.46	3.52	0.67	0.78
SF	small	94.50	1.35	1.10	small	

[Notes] BFS: Blast furnace slag, PS: Phosphate slag,
QS: Quartz sand, SF: Silica fume.

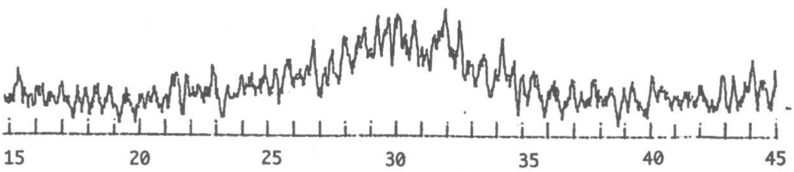
2.2 MATERIALS AND CHARACTERISTICS

(1) Cement

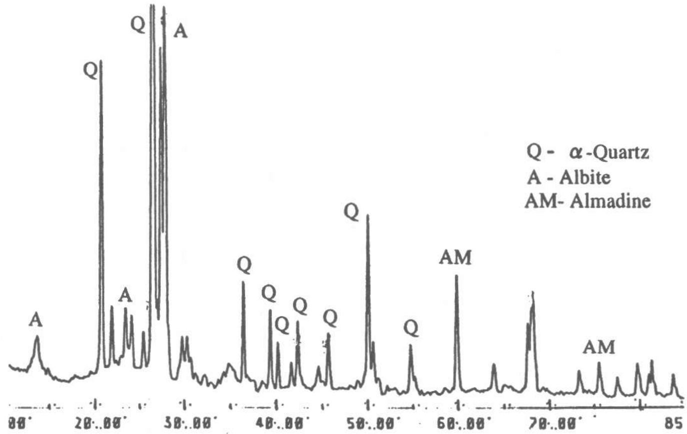
Ordinary portland cement was used in the experiment, with Blaine specific surface area of 3420 cm^2/g,



Diffraction angle (°2 θ)
(a) Blast furnace slag



Diffraction angle (°2 θ)
(b) Phosphate slag



Diffraction angle (°2 θ)
(c) Quartz sand
Fig.2 XRD profiles of powders

the chemical composition of which are shown in **Table 1**.

(2) Superfine powders

a) Chemical composition

Chemical composition of the powders are shown in **Table 1**. The original state powder is silica fume (SF), and other powders are manufactured by grinding technologic process. Blast furnace slag (BFS), phosphate slag (PS) and quartz sand (QS) were ground to given fineness respectively with a ball mill.

b) Phases of the powders

X-Ray Diffraction patterns of the powders are shown in **Fig.2**. A X-Ray of CuK α radiation (λ =1.54 Å) was used in the process. The patterns indicate that both BFS and PS are vitrescence, while QS is a crystalline material with main component α -quartz crystal. The other phase constituents are shown by some weak peaks in **Fig.2** (c) are albite and almadine crystal etc. In regard to the silica fume, a lot of studies have shown that it consists of amorphous SiO_2 [1, 2].

c) Fineness of the powders

Fineness of the powders made from BFS, PS and QS are all same , with specific surface area 6500 cm^2/g. But for silica fume, powder in original state, and with specific surface area $2\times10^5 cm^2/g$ was used.

(3) Superplasticizer

Powdery naphthalene sulfonic superplasticizer(NS) was used.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 FILLING EFFECT AND DISPERSING EFFECT OF POWDERS

The fluidity experiment of the cement pastes with powders were carried out, and the experimental results are shown in **Fig.3**. Cement pastes contain the powders with 0, 5, 10, 20 and 30% separately, and each one was given a water to binder ratio 0.29 and added 0.9% of NS also. the cement paste without powder was referred as a control. It can be seen that the flow values of pastes with an appropriate amount of the powder are higher than that of the control, especially in case of BFS and PS. Furthermore, the flow value increased continuously with increasing of powder content of BFS and PS. For 30% replacement of cement, the flow value of pastes with BFS and PS is up to 285mm and 280mm, respectively, while the control paste is only 240mm. Nevertheless, the flow value of paste blended QS powder increases slightly. Although the paste containing SF increases to a certain degree, the tendency of decline appeares when SF content is beyond 5%.

The experiment results indicate that the fluiding effect of BFS and PS is much higher than that of QS and SF. It is evidenced that vitrescence and non-vitrescence powder must work in different mechanism. To clarify the role of the powders in the pastes, the flow values of each individual powder paste were taken, before and after adding of NS (dosage 0.9%). Except that SF paste was given a W/B 0.45, the others were prepared with W/B 0.3. As to SF, for huge

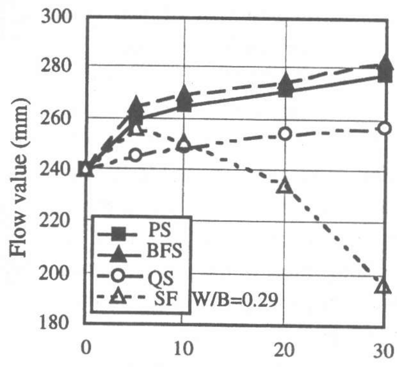


Fig.3 Fluidity of cement paste with powder

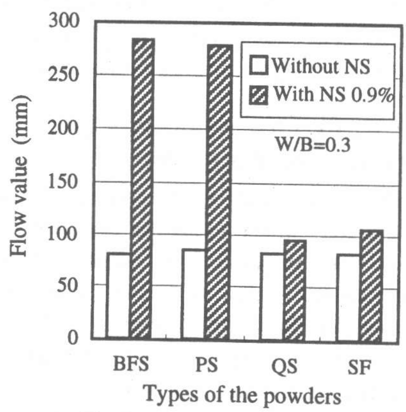
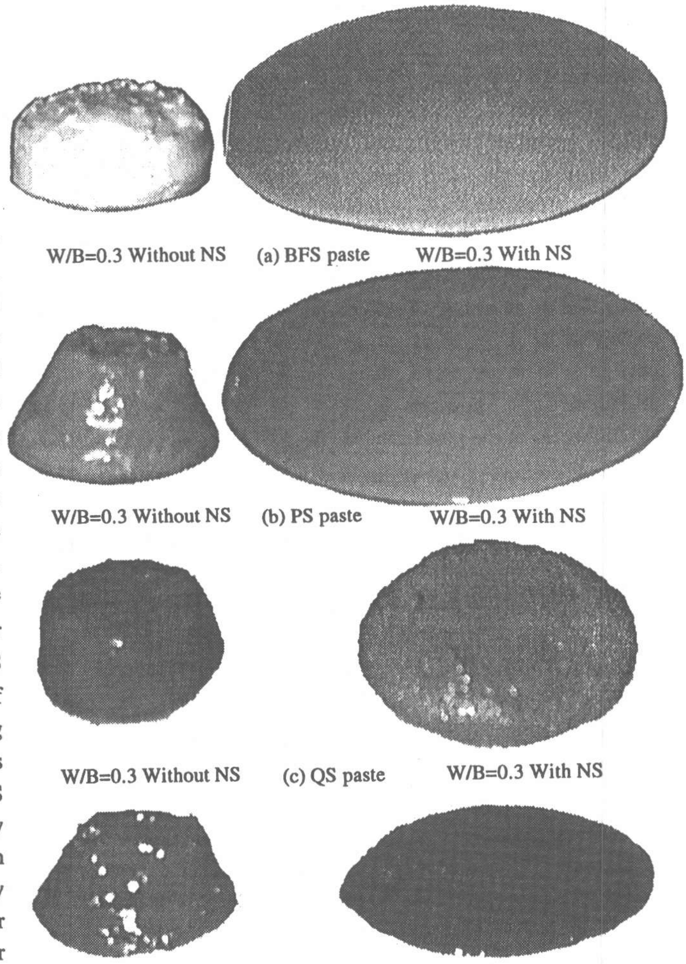


Fig.4 Fluidity of powder pastes

surface area and more water adsorption on the surface, it was given a higher W/B ratio, with which SF paste was identical to the others in consistence before adding NS. What is noticeable is that the pastes of individual BFS and PS exhibit a very remarkable fluidity after added of NS. For instance, BFS: flow value 80mm without NS to 285mm with NS, and PS: flow value 85mm without NS to 280mm with NS. The flow values and flow state of the powder pastes are shown in **Fig.4** and **Fig.5**. This phenomenon means that the particles of vitrecence powder themself adsorb NS, and produce the dispersing force to particles of cement and powder. This action should be called the dispersing mechanism. On the other hand, for pastes of SF and QS powder, there was little increment of the fluidity of paste in spite of dosing NS. However, when the cement was partially replaced with SF or QS powder, the paste gained in fluidity to some extent. This phenomenon could be considered to be caused by the filling effect of the powder rather than the dispersing effect. In other words, grains of QS powder or silica fume in the paste may occupy spaces among cement particles where otherwise can be occupied by mix water. Thus the water involved in flocculation structure could be released, which causes some gain in fluidity of the paste. This is the filling mechanism we have known [1, 3].



W/B=0.3 Without NS (a) BFS paste W/B=0.3 With NS

W/B=0.3 Without NS (b) PS paste W/B=0.3 With NS

W/B=0.3 Without NS (c) QS paste W/B=0.3 With NS

W/B=0.45 Without NS (d) SF paste W/B=0.45 With NS

Fig.5 Flow state of powder pastes

3.2 ELECTRICAL ASPECTS OF SURFACE OF VITRESCENCE POWDER

As mentioned above, the vitrescence powders themself could adsorb NS, which means that the particles of powder have electrostatic surface. As we have known, the vitrescence materials are formed by cold quenching melted slag, which prevented it from crystallization. Instead of complete stereo structure of crystalline, a great deal of silica oxygen tetrahedrons with free ends were generated. At the end of which chemical bonds were in dangling bond state. And consequently surplus

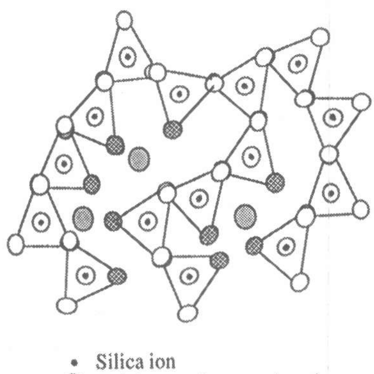


Fig.6 Microstructure of vitrescence

electrovalence comes to in presence as shown in **Fig.6**. As the material was ground to the very fine state, the surplus electrovalence were exposed on the surface of particles, so that the surface energy of the powders was very high. Since superplasticizers are all surface active agents, which could balance surplus electrovalence and lower the surface energy of the particles. So NS was adsorbed on the surface of the powder particles as soon as the powder particles were encounted with it, when the pastes were prepared. This physical chemistry action produces a strong electrostatic repulsion and induces the dispersing effect to the paste. As to both crytstalline and amorphous powder, however, without the free ends carrying surplus electrovelence, a remarkable adsorption of NS could not occur. A crystalline powder made from grinding technologic process or an amorphous powder obtained through other technologic process, could also get some enhancement of surface energy, but it is much lower than that of vitrescence powders. So they are not capable of adsorbing NS significantly and producing the dispersing action to cement paste as the vitrescence powders do.

3.3 LOWEST CRITICAL DOSAGE OF NS

In view of the previous discussion on the fluiding effect of powders, the vitrescence powder is very beneficial to enhance the fluidity of paste. However, that is not always the case. As shown in **Fig.7**, in absence of sufficient dosage of NS, the flow value of the cement paste with the powders is lower than that of the control paste. The water to binder ratio for all pastes here was 0.29. The experiment results confirmed that vitrescence powders are of flocculence characteristic, attributing to electrostatic surface of particles. For higher fluidity of fresh concrete, the critical dosage of superplasticizer should be taken into consideration. The critical dosage is the minimum superplasticizer required, with which side-effect of flocculence can be eliminated, and the flow value of paste with powder becomes equal to the control paste. When the addition of superplasticizer is beyond the critical dosage, the increase ratio of fluidity of cement paste with the powder is much higher than that of the control paste. In manufacturing high performance concrete and high fluidity concrete, the characteristic of vitresence powder would be very crucial.

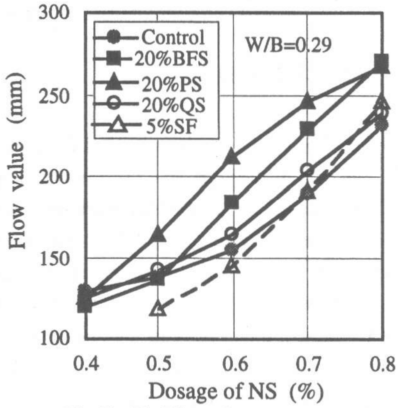


Fig.7 Fluidity of cement paste containing powder with NS

3.4 VARIATION OF VISCOSITY AND YIELD STRESS OF CEMENT PASTE WITH POWDERS

For the viscosity test, the pastes with and without powders were prepared, and the water to binder ratio was kept constant at 0.29. Each comparison group was with same dosage of NS. Taking the cement paste without powder as a control, and in other pastes, we replaced the cement partially with 20% BFS, PS and QS, and 5% SF, respectively.

With the viscometer the stress of each specimen was measured at different rotation speeds of 0.5, 1, 2.5, 5 and 10 r/s, and the experiment data were analyzed in linearity regression method. The viscosity and yield stress values obtained from the analysis are shown in **Fig.8 and Fig. 9**. The experiment results

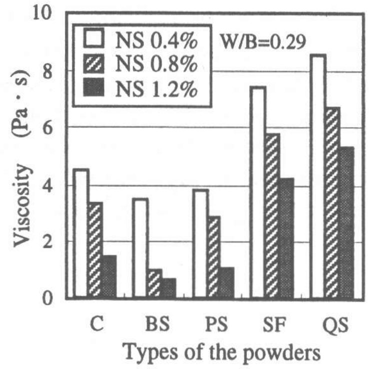


Fig.8 Viscosity variation with powders

indicate that the pastes, with partial replacement of cement by vitrescence powder, exhibit both viscosity and yield stress lower than the control paste. As to the pastes with non-vitrescence powders, all viscosity and yield stress values are higher over the control. These different behaviors convey certain relations with the surface electrovalence of the vitrescence powder. Compared with the cement, whether vitrescence or non-vitrescence powder has rather larger surface area , and more water adsorption on the surface , which can induce consistence gain of the paste (Tending to cohere). In the paste with vitrscence powder, the consistence gain would be overcomed by the dispersing effect of the powder, and the paste would be fluidized. While incorporating non-vitresence powder in the paste, without accompanied by dispersing effect, make the paste more cohesive and conglutinate in comparison with the control paste.

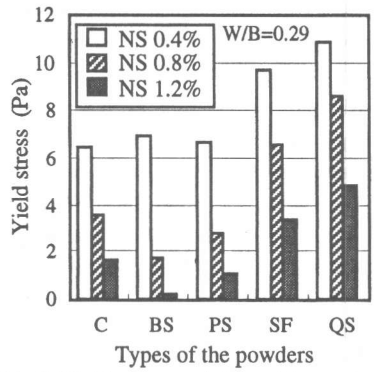


Fig.9 Yield stress variation with powders

4. CONCLUSIONS

Basing on the experimental study mentioned above, the following conclusions could be drawn :

1) The role of the superfine powders in the paste was clarified through this experimental study. Vitrescence powder and non-vitrescence powder are characterized in different fluiding mechanism. The former is relied on the dispersing effect, and the latter on the microfilling effect. Even if the vitrescence powders have the filling effect also, the disersing effect plays a predominant role in enhancing the paste fluidity .

2) For vitrescence powders with the given fineness, magnitude of dispersing action depends on the quantity of free ends of silica oxygen tetrahedrons, which was determined mainly by cold quench condition. It is essential to work still further on the relationship between the dispersing effect and the microamorphas .

3) As compared with the control paste, the cement pastes with vitrescence powder exhibit lower value in the viscosity and the yield stress, but with the non- vitrescense make the both values higher.

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