The preparation of solid acid and acid water reducing agent for slag is prepared by adsorption method

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Abstract. Solid polycarboxylate superplasticizer can not only solve the problems caused by water reducing agent in storage and transportation, but also meet the needs of some special projects. We can choose to use the mineral slag, which is larger than surface area and has stronger adsorption, as adsorbent to absorb liquid polycarboxylate superplasticizer and absorb its moisture, and then makes solid polycarboxylate superplasticizer after drying. It determines the solid-liquid ratio to prepare the solid polycarboxylate superplasticizer to be 3:1. The temperature change within 100°C will not cause changes in the functional group and structure of the water reducing agent molecule. The application of the solid polycarboxylate superplasticizer was basically unchanged compared with its liquid water reducing agent.

1. Introduction

Recent years, polycarboxylate superplasticizer with high function has gained rapid development, but what the current domestic market sells is still the liquid polycarboxylic acid with the solid content from 20% to 40%. While the liquid has very big disadvantage in transportation, storage and other aspects compared with the traditional naphthalene water reducing agent, which greatly limits the development of polycarboxylic acid. The proposal of solid polycarboxylate superplasticizer (solid polycarboxylate superplasticizer, abbreviated as SPC) concept [1], not only can solve the problems caused by water reducing agent in storage and transportation, but also meet the needs of water reducing agent use in the engineering technology field, such as dry-mixed mortar, sprayed concrete and high-grade ceramic.

At present, the common methods for preparing solid polycarboxylate superplasticizer are spray drying method, precipitation method, adsorption method and direct synthesis of high solid content polycarboxylate superplasticizer [2]. The molecular of polycarboxylate superplasticizer was easily cohered, leading to the damage of the polycarboxylate superplasticizer’s microstructure and its application performance is affected by spray drying method. Most of the Precipitation in precipitation method is polymer organic matter, which can not avoid bringing certain pollution to the environment; And the polycarboxylate superplasticizer after direct synthesis has certain moisture content, but not achieve full solid powder, and direct synthesis method has the complicated process, so it is not convenient for mass production. Adsorption method refers to borrowing some strong adsorption materials as adsorbent, by adsorption of the effective components in liquid polycarboxylate

superplasticizer and absorbing the moisture at the same time, thereby solid polycarboxylate superplasticizer is prepared. Hai-jun Zhao of southwest university of science and technology [3] and others use fly ash as adsorbent to make the solid polycarboxylate superplasticizer and obtained relatively good results. However, the adsorption quantity of fly ash to effective ingredients of polycarboxylate superplasticizer is big, so there is no doubt that it will affect the performance of the polycarboxylate superplasticizer in a certain degree.

Slag, as a traditional industrial waste residue, the surface is rough, is easy to absorb moisture. In order to increase the utilization rate of the slag and achieve the goal of green environmental protection, this study use slag as adsorption material, to adsorb liquid polycarboxylate superplasticizer molecules and the moisture, and then through some simple processing, can make polycarboxylate superplasticizer solid and keep its various application performance will not decline.

2. Intruction and experiments

2.1. Main raw materials
Cement:portland reference cement made in Qufuzhonglian cement company,product type P·I 42.5.
Water reducer: there are three types of Polycarboxylic acid liquid high efficiency water reducer PC3600, PC4000, PC5000 and PC8000 in this experiment.These mother liqutor are all provided by Beijing Construction Engineering Research Institute, whose solids content is about 40%. Markthem 1#, 2#, 3#and 4# to make it convinintly in the further research.
Slag:the slag of the experiment is produced by shunxin mineral processing factory, whose apparent density is not more than 2.5g/cm³, water is not more than 1%, hydrophilic coefficient is not more than 1%.

2.2. Major equipment and instruments
Nocletis-5 infra-red sepctrometere, f-700 uttraviolet sepctormeter, DSC2000F3 differencial scanning, FA2004 analytial balance, TGL-16C lentrifuge, 101-1AB eletrothemal blowing dry box, cement pasate mixer.

2.3. experiment and test method

2.3.1. Preparation method of solid polycarboxylic acid water reducing agent
(1)The slag and liquid high efficiency polycarboxylic acid reducer are mixed in a certain proportion, and the water in the liquid PC is removed by vacuum.
(2)Place it in the slag water reducing agent of mixture in the oven, set above a certain temperature dry for several hours (specific drying time required depends on the actual situation of material is dry), thoroughly remove liquid entrainment in the poly carboxylic acid water reducing agent of water, which made solid PC products.

2.3.2. Measurement of adsorption capacity of polycarboxylate superplasticizer. According to take a certain amount of adsorbent in the beaker, add a certain concentration of water reducing agent solution (to calculate the initial concentration of water reducing agent C₀), stirring after 3 min, let stand for a certain time, take the supernatant, centrifuge separation 10 min, dilute liquid isolated make it conform to the concentration range of beer's law, use ultraviolet spectrophotometer absorbance measurement, through the work curve to determine the balance of the remaining water reducing agent concentration C, according to the formula to calculate the adsorption quantity in the literature [4].

\[ \Gamma = \frac{(C₀ - C)V}{m} \]

In the formular: \( \Gamma \) — adsorption capacity, mg•g⁻¹; \( V \) — solution volume, ml; \( m \) — adsorbent quality, g; \( C₀ \) — initial concentration of water reducer, g•l⁻¹; \( C \) — equilibrium concentration of water reducing agent, g•l⁻¹.
3. Experiment result an disussing

3.1. The liquid slag adsorption of polycarboxylate superplasticizer on the surface

(1) Adsorption isotherm of liquid polycarboxylate superplasticizer

According to the mass ratio, slag: liquid polycarboxylic acid water reducing agent = 1:10 solid-liquid ratio, respectively to four kinds of liquid gathered in the sour water reducing agent in a beaker, according to the 1.3.2 method test water reducing agent on the surface of the slag, adsorption capacity, the result is shown in figure 1.

![Figure 1. Isothermal adsorption curve of water reducer](image1)

![Figure 2. Adsorption kinetics curve of 2# water reducer on slag surface](image2)

FIG. 1 shows that the saturation adsorption capacity of four types of liquid polycarboxylic acid reducers on the slag surface is different, which is related to the molecular weight of the water reducer and its structure [5]. The molecular weight of the four water reducers was PC5000 < PC4000 < PC8000. Among them, PC3600, PC5000 and PC8000 are ether type polycarboxylic acid reducers, and the stronger the adsorption capacity of water-reducing agents with the larger molecular weight of the same structure, the highest saturation adsorption capacity of PC8000. PC3600 is similar to PC4000 in formula weight; while PC4000 is the lipid-type polycarboxylic acid reducer, and lipid-like polycarboxylic acid reducer is generally more adsorbed than ether type polycarboxylic acid reducer. Therefore, PC4000 saturation adsorption is larger than PC3600. Saturated adsorption amount on the big shows that adsorbent water reducer molecular adsorption ability is strong, strong adsorption can make water reducer molecules application performance influenced by a certain degree, thus the preparation of SPC should choose small saturated adsorption amount of adsorbate and adsorbent, and 2 # and 3 # saturated adsorption amount is small, due to the 2 # water reducer is more stable, the next research will choose 2 # poly carboxylic acid water reducing agent as the research object.

(2) The adsorption kinetics curve of PC on slag surface

Take a concentration of 0.5 mg/L of 2# water reducer, Using the method of determination of the adsorption quantity in the 3.1.2, drawing on adsorption quantity of adsorption time, the water reducing agent on the surface of the slag powder, the adsorption kinetics curve, as shown in figure 2.

It can be seen from figure 2 that as the reaction time increases, the adsorption capacity of the water reducer will gradually increase and approach to a saturation value. During the initial stage of 0 ~ 20min, the adsorption capacity of the water reducer increased sharply, then remained relatively stable, and then gradually increased to saturation adsorption. The rapid increase of adsorption capacity at the beginning can be considered as the addition of PC water reducer. Due to its high electronegativity, the adsorbents and the surface adsorption of early hydration products will be quickly absorbed and electrostatic repulsion will be generated. The relatively stable stage may be following an adsorbent hydration system of spherical particles can cause desorption and water reducing agent, at the same time the new hydration products can produce shielding effect to water reducing agent adsorption layer and the adsorption quantity is relatively stable; Subsequent increase slowly to the saturated adsorption phase, generally considered until almost completely with the increase of hydration degree of hydration,
hydration products keeps increasing, the adsorption quantity will increase slowly to the saturated adsorption amount[6].

3.2. The effect of solid-liquid ratio on water reducing agent

Take appropriate amount of the solid-liquid ratio of 1:1, 2:1, 3:1 and 4:1 respectively, under the condition of 100℃ drying of SPC (PC of effective components account for 0.6% of the cement content) into a stirring pot. According to GB/T 8077-2000 making the flow test and the results are shown on table 1:

As is shown on the table, it has no difference comparing with liquid water reducer, is indicated that solid polycarboxylic Superplasticizer still retains the solid water reducing agent of the original liquid, and the net slurry flow and the water reducing agent improve the fluidity of the cement.

Because of the slag powder particle size is small, mixed with cement paste after can give full play to its physical close-grained filling effect, can replace more cement filling water between particles, so that the slurry fluidity stronger. Moreover, the content of cement clinker in the slurry is lower, and the content of the corresponding early hydration products can be reduced[7]. Because the water slurry is formed by cement particles suspended in water medium, the viscosity depends not only on the medium viscosity, solid particles and its acting force between itself and water, but also related to of hydration reaction of cement, mixed material. The hydration reaction occurs immediately after the cement is added to the water, and the resulting hydrated products are connected to each other, which increases the viscosity of the cement slurry. Because the hydration reaction rate of cement is more rapid than that of mineral powder, the higher the amount of mineral powder, the lower the viscosity of the slurry, the better the liquidity. However, due to the small amount of slag powder added in this experiment, the net slurry flow rate of slag powder has influence on cement, but it is not obvious. However, considering the convenience of subsequent drying treatment, the solid-liquid ratio was 3:1.

3.3. The effect of drying temperature on the structure of water reducer

Confect SPC as the solid-liquid ratio 3:1, making the infrared spectrum tests under the temperature of 65℃, 80℃ and 100℃ respectively after drying, the results are shown in figure 3, 4, 5.

Table 1. The effect of solid liquid on cement paste

| solid liquid ratio | Fluidity/mm |
|-------------------|-------------|
| blank group       | 182         |
| liquid group      | 270         |
| 1:1               | 270         |
| 2:1               | 272         |
| 3:1               | 276         |
| 4:1               | 276         |

Figure 3. Infrared spectra of SPC dried under 65℃
We can see from the figure 3, 4, 5, at 65℃, 80℃ and 100℃ drying temperature, the structure of the solid water reducer did not change, so basically can think within 100℃ drying temperature of water reducer, water reducer basic molecular structure remains the same. As you can see, also be slag liquid after absorption of poly carboxylic acid water reducer, its functional group compared with the original liquid poly carboxylic acid water reducer did not change, only the width of the absorption peak and some changes have taken place in intensity. We can say that under the experimental condition, when the liquid poly carboxylic acid water reducing agent is slag its structure does not change after adsorption, thus the performance of the original liquid poly carboxylic acid water reducing agent and should be able to get good protection.

3.4. The application of solid water reducer
Drying it under 100℃, the solid state polycarboxylate superplasticizer with a solid to liquid ratio of 3:1 was added to the cement paste with a water cement ratio of 0.5 at the ratio of 0.5%, 1%, 1.5% and 2% to obtain the setting time as shown in table 2.
Table 2 Effect of slag solid water reducer on initial setting time of cement

| Dosage of solid water reducer/% | initial setting time/min | final setting time/min |
|--------------------------------|--------------------------|------------------------|
| blank group                    | 184                      | 273                    |
| 0.5 (liquid)                   | 310                      | 417                    |
| 0.5                            | 300                      | 405                    |
| 1                              | 294                      | 406                    |
| 1.5                            | 289                      | 397                    |
| 2                              | 291                      | 400                    |

From the table 2 we know that, having mixed with SPC, the initial setting time and final setting time will be reduced slightly compared with the addition of 0.5% liquid polycarboxylate superplasticizer. Usually the slag cement paste mixed with a certain amount of the setting time should be the growth of [8], due to the addition of slag powder in this study is not very high, so when the powder added is not many, in this composite cement-slag system, will reduce the amount of cement, effective water cement ratio rose water the increase rate of cement and slag; because of its initial activity level is not low, and has a compact complementary role, the setting time of cement paste is reduced.

Put into the concrete with water cement ratio of 0.4 and sand ratio of 31%, in the ratio of 0.5%, 1%, 1.5% and 2% according to the strength test of GB/T50107-2010, the results of table 3 were obtained.

Table 3 Effect of slag solid water reducer on strength of concrete

| Dosage of solid water reducer/% | compressive strength/MPa | Flexural strength/MPa |
|--------------------------------|---------------------------|-----------------------|
|                                | 7d                        | 28d                   |
| blank group                    | 23.2                      | 41.5                  | 7.2        |
| 0.5 (liquid)                   | 25.1                      | 53.5                  | 8          |
| 0.5                            | 24.6                      | 53.9                  | 8.3        |
| 1                              | 24.8                      | 54.3                  | 8.5        |
| 1.5                            | 24.3                      | 54.8                  | 8.8        |
| 2                              | 24.5                      | 55.1                  | 9.2        |

It can be seen from table 3, pure liquid polycarboxylate superplasticizer 7d strength is lower than the compressive strength of concrete doped 7d solid reducing agent, the 28d compressive strength and flexural strength is slightly higher than that of liquid polycarboxylate superplasticizer.

In general, the use of slag solid polycarboxylic acid reducer has no significant effect on concrete performance, and is basically unchanged compared with its liquid water reducer.

4. Conclusion
(1) The saturation adsorption capacity of four liquid polycarboxylic acid reducers was PC8000 > PC4000 >> PC5000. The higher the molecular weight of the same type of water reducing agent, the stronger the adsorption capacity; The molecular weight is similar, and lipid-like polycarboxylic acid reducer is generally better adsorbed than ether type polycarboxylic acid reducer.
(2) The solid-liquid ratio of the solid polycarboxylic acid reducer was determined by the experiment is 3:1.
(3) Under 100 °C drying slag water reducing agent, the basic molecular structure remains the same.
(4) The use of slag solid polycarboxylic acid reducer has no great effect on concrete performance, and it is basically unchanged compared with its liquid water reducing agent.
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