Study on Adsorption Properties of Naphthalene Sulfonic Acid Formaldehyde Condensate Dispersant

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Abstract. Concrete water reducer is one of the indispensable components of modern concrete. Naphthalene sulfonate acid formaldehyde condensate (FDN) has the characteristics of high water reducing rate, no air entrainment and good adaptability of cement. FDN is one of the most widely used water reducing agents in commercial concrete. The dispersion of water reducer is achieved by adsorbing on the surface of solid particles. In this paper, FDN was synthesized from the laboratory. The molecular structure of FDN was analyzed by infrared spectrum. The variation of FDN adsorption capacity with FDN concentration and adsorption time was analyzed by ultraviolet spectrum. The adsorption behavior of FDN on the surface of cement particles was investigated and its adsorption performance was studied.

1. Introduction

By means of polar adsorption and repulsion, concrete superplasticizer can reduce the gravitational attraction between cement particles and disperse them, thus achieving the effect of water reduction. The purpose of using water reducing agent is to improve the strength, workability, frost resistance, impermeability and corrosion resistance of concrete [1].

Cement water reducer is the most widely used cement additive at present. After adding a small amount of water reducer (generally 0.2%-1.5% of cement weight) into cement concrete, the water consumption of concrete can be reduced by 5%-25%, the workability of concrete can also be improved, and the amount of cement per unit can be reduced by 5%-20%. Thus, the strength of concrete at early or late stage can be greatly improved. Therefore, it can be used as one of the important means to improve various properties of cement concrete. Retarded high-strength concrete and early-setting high-strength concrete can be prepared by adding water reducers with different properties to ordinary cement. This method is more economical, simple and flexible than developing and using special cement [2,3].

More than 80% of the superplasticizers used in modern concrete are naphthalene series superplasticizers. As the most widely used cement additive, naphthalene series water reducer still has some shortcomings such as segregation, slump loss and poor adaptability to some cement. Therefore, it is very necessary to investigate the adsorption behavior of FDN on the surface of cement particles to improve the adsorption performance of naphthalene series water reducer [4].

In this paper, FDN was synthesized from laboratory. The molecular structure of FDN was analyzed by infrared spectrum. The variation of FDN adsorption capacity with FDN concentration and adsorption time was analyzed by ultraviolet spectrum. The synthesis process, basic structure and adsorption properties of FDN on the surface of cement particles were studied.
2. Experimental part

2.1 Synthesis of FDN

2.1.1 Experimental drugs
Naphthalene, concentrated sulfuric acid, formaldehyde, NaOH, CaCO₃

2.1.2 Experimental steps
(1) 12.8g naphthalene (0.1mol) was weighed and placed in four flasks. When the temperature was raised above 130℃, 98% concentrated sulfuric acid (about 7mL, 0.13mol) was slowly dripped under stirring.

(2) After adding acid, the temperature will continue to rise to 160℃-170℃ and constant temperature for 2 hours. When the temperature is lowered to 110 ℃, add 4 mL -5mL distilled water. Under stirring, take 2-3 drops of solution with a glass rod and determine the solution pH.

(3) Adjust the temperature, and when the temperature is between 80℃ and 90℃, 10 mL (0.3 mol) 37% formaldehyde solution is dripped slowly. When the temperature rises to 95℃-100℃, stir for 5-6 hours at constant temperature, add 30 mL hot water and stir until all dissolve.

(4) Add 3.6g (0.09mol) NaOH concentrated solution, then slowly add CaCO₃ powder soaked in water, stirring at the same time until no bubbles are produced, determine the solution pH at about 7.

(5) Filtration, collection of filtrate, concentration, drying, grinding to a light brown powder product [5,6].

2.2 Analysis of FDN Infrared Spectrum
The group characteristics of FDN were determined by FTIR-8400S Fourier transform infrared spectrophotometer. The basic determination methods were as follows: 200 mg dried KBr were grinded uniformly in agate grinding. KBr powder is put into the die for pressing. Then the sample solution was smeared on the KBr tablet and put into the light path. Scanning range 400-4000cm⁻¹, using KBr tablet as a reference, the infrared spectra of the sample was obtained as shown in Fig. 1.

![Infrared spectra of naphthalene sulfonic acid formaldehyde condensate](image-url)
It can be seen from the infrared spectra of FDN in Fig. 1, the absorption peak of 3440 cm\(^{-1}\) is the stretching vibration of -OH group. The absorption peak of 3050 cm\(^{-1}\) is the stretching vibration of naphthalene ring =C-H. 1633 cm\(^{-1}\) and 1597 cm\(^{-1}\) are the absorption peaks of naphthalene ring skeleton vibration. 890 cm\(^{-1}\) and 830 cm\(^{-1}\) are the absorption peaks of bending vibration of solitary hydrogen and two adjacent hydrogens on naphthalene rings. 2920 cm\(^{-1}\) is the stretching vibration absorption peak of methylene hydrocarbon bond. 1450 cm\(^{-1}\) is the bending vibration absorption peak of methylene hydrocarbon bond. 1360 cm\(^{-1}\) and 1040 cm\(^{-1}\) are the absorption regions of sulfonate \[^{[7]}\].

Therefore, FDN contains -OH group, naphthalene ring = C-H, methylene group and sulfonic acid group.

2.3 Determination of adsorption property of FDN on cement particles surface

2.3.1 Drawing Standard Curve

1 g/L FDN solution was prepared and diluted to 0.01 g/L. Then, based on 0.01 g/L FDN solution, 100 mL volumetric flask was respectively diluted to 0.0025 g/L, 0.002 g/L, 0.001 g/L, 0.00125 g/L and 0.0005 g/L. The absorbance at different concentrations was measured by ultraviolet-visible spectrophotometer, and the standard curve was obtained as shown in Fig. 2.

![Fig. 2 Standard curve diagram of FDN absorbance varying with concentration](image)

In the formula (1): \(n^s = V(C_0 - C)/m\)

2.3.2 Determination of adsorption performance of FDN with adsorption time

80 mL 0.0025g/L FDN solution was poured into 250 mL conical bottle, and 1.0422 g cement was added. Stir the mixed solution and separate into layers. The supernatant was taken. The changes of absorbance with adsorption time after 0 minutes, 10 minutes, 20 minutes, 30 minutes, 40 minutes, 50 minutes and 60 minutes were measured by ultraviolet-visible spectrophotometer. The amount of adsorption was calculated according to Fig. 2 and formula (1).

The characteristic peak at 272 nm was selected to determine the changes of absorbance after 0 minutes, 10 minutes, 20 minutes, 30 minutes, 40 minutes, 50 minutes and 60 minutes of adsorption. The curve of adsorption capacity with adsorption time was shown in Fig. 3.
Fig. 3 The curve diagram of FDN adsorption capacity change with adsorption time

Fig. 3 shows that the adsorption rate of FDN on the surface of cement particles is very fast in the first 30 minutes, and obviously slows down after 30 minutes. It is concluded that FDN mainly adsors small molecules in cement voids within 30 minutes before adsorption, while some large molecules adsorb on the surface of cement particles, the adsorption tends to be saturated within 30 minutes. Small molecules in the voids begin to be covered by hydration products, and then begin to adsorb on the surface of hydration products after 40 minutes, which increases adsorption capacity [8,9].

2.3.3 Determination of adsorption property of FDN with concentration change

0.0025 g/L, 0.002 g/L, 0.001 g/L, 0.00125 g/L, and 0.0005 g/L FDN solutions were placed in five 250 mL conical flasks. 1.0023 g, 1.0141 g, 1.0052 g, 1.0032 g and 1.0421 g cement were added to the conical flasks. Mixing, standing and taking supernatant separately. After adsorption 20min, the absorbency of FDN solution was measured by ultraviolet-visible spectrophotometer. The adsorption capacity was calculated by formula (1). The curve diagram of FDN adsorption capacity with concentration is shown in Fig. 4.

Fig. 4 The curve diagram of FDN adsorption capacity with concentration after adsorption 20 minutes

Fig. 4 shows that the amount of FDN adsorbed on the surface of cement particles increases rapidly with the increase of solution concentration. The analysis shows that the adsorption of FDN on the surface of cement particles is manifested by monolayer adsorption [10].
3. Conclusion
Naphthalene sulfonic acid formaldehyde condensate (FDN) has a certain adsorption performance on the surface of cement particles, and its adsorption capacity is closely related to the FDN concentration and adsorption time. The adsorption of FDN on the surface of cement particles is manifested by monolayer adsorption.

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