Study on the Determination Method of the Adsorption of Water Reducer on Cement Surface Based on Total Organic Carbon Analyzer

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Abstract—At present, most of the methods for testing the amount of Water-reducing admixture adsorbed on the surface of the cement particles use the total organic carbon method (TOC method), but various literatures describe the pre-treatment of the test method as ambiguous and poor operability. In view of the above problems, this paper carried out a study on the pre-treatment conditions of the test for the adsorption of Water-reducing admixture on the surface of cement particles by total organic carbon method, and explored the effects of stirring time, standing time, and standing temperature on the adsorption of Water-reducing admixture on the surface of cement particles. The study determined the pre-treatment and test conditions of the TOC method, and provided reference for the research on the adsorption behavior of the water reducer on the surface of cement particles. The correlation coefficients of the standard curve of Water-reducing admixture obtained by this method are all greater than 0.999, the relative error of the results of the 10 parallel experiments of the method is less than 0.005%, and the relative standard deviation (RSD) is 0.7706%.

1. INTRODUCTION

Water-reducing admixture is widely used in concrete engineering as "industrial MSG". Through the application of concrete Water-reducing admixture, the performance of fresh concrete or hardened concrete can be effectively improved and the overall performance of concrete can be improved. Adsorption is the first step in the interaction between the Water-reducing admixture and the gel particles, and it is also the basis for other interface physicochemical effects. The Water-reducing admixture is added to the concrete mixture, and the first interaction with the cementitious material is adsorption. Through the adsorption, the water-reducing function of the Water-reducing admixture is dispersed. In order to study the adsorption behavior of the Water-reducing admixture on the surface of the cement particles, we need to determine the amount of Water-reducing admixture adsorbed on the surface of the cement particles. Common methods for determining the amount of Water-reducing admixture adsorption include ultraviolet-visible absorption spectroscopy orga¹³.

In 1992, H. Uchikawa et al. first studied the adsorption characteristics of lignin sulfonate and naphthalene sulfonate water reducers on the surface of single cement ore. In 1999, Hanehare et al. studied...
the adsorption behavior of naphthalene-based and polycarboxylic acid Water-reducing admixtures on the surface of cement particles. At present, the measurement methods of adsorption amount mainly include ultraviolet-visible absorption spectroscopy (UV-Vis), organic oxygen consumption method (COD) and high-performance liquid chromatography (HPLC). Among them, ultraviolet-visible absorption spectroscopy is the most commonly used method to determine the amount of Water-reducing admixture adsorption. However, there is a certain error in the determination of PC adsorption by this method. The possible reasons for research and analysis are: (1) When using the ultraviolet spectrophotometer to test the absorption characteristic peak of PC, the characteristic peak will shift to a certain extent as the concentration of PC varies. Affects the formulation of the standard curve; (2) There are some fine particles in the filtrate after stirring and centrifugal suction filtration, which will make the filtrate exhibit a certain colloid Tyndall effect, and the light wave is scattered by these small particles, so that the measured result will be greater than the actual value, resulting in The calculated adsorption amount shows a negative value. In 2002, Yoshioka et al. used TOC to quantitatively analyze the adsorption capacity of polycarboxylic acid Water-reducing admixture on the surface of each cement single ore. This method was used to test the accuracy of the adsorption of polycarboxylic acid Water-reducing admixture in cement. And stability are better. oxygen consumption and total organic carbon (TOC) [4-5]. However, due to the existing data, there is little mention of the specific operation of the TOC method for determining the amount of Water-reducing admixture adsorbed on the surface of the cement particles. How to deal with the test sample, how to show the test results, etc. Are lack of experimental data support. To this end, this paper establishes a test method suitable for characterizing the adsorption of Water-reducing admixture in cement (concrete) by studying the pre-treatment conditions of the test method, the preparation of the test solution, and the conditions for making the standard curve. It is helpful to investigate and study the adsorption behavior of Water-reducing admixture on the surface of cement particles and the mechanism of action.

2. EXPERIMENTAL PART

2.1 Main instrument
Vario TOC total organic carbon analyzer (Elementar trading(shanghai) Co., Ltd.) instrument working conditions are shown in Table 1; electronic analytical balance, accuracy 0.0001 g; ultra-pure water machine, Ultra series ultra-pure water machine; high-speed desktop centrifuge, (TGL-108) produced by Shanghai Anting Scientific Instrument Factory.

| Detector  | Catalyst                  | Tem (°C) | System pressure (mbar) | Carrier gas flow rate (mL/min) |
|-----------|---------------------------|----------|------------------------|-------------------------------|
| NDIR      | Pt Composite catalyst     | 850      | 1100                   | 200                           |

2.2 Reagents and raw materials
Phosphoric acid (analytical purity). Sodium carbonate (analytical purity), potassium hydrogen phthalate (reference reagent). Min fu cement (PO 42.5). Red Lion cement (PO 42.5R). water reducer S10E (solid content 52.89 %). Water reducer S08F (solid content 50.97 %).

2.3 Experiment procedure
Determine the solid content of the sample according to GB/T 8077 " Methods for testing uniformity of concrete admixture "[6]. Calculate the sample weight X g required to prepare the sample solution with 1 L concentration of 2.5 mg /L, accurately weigh the X g sample into a 300ml beaker, and transfer all the samples into a 1L volumetric flask for volume determination after complete dissolution. Shake well to obtain the sample solution B. Stepwise dilution the sample solution into 2.5 mg/L, 1 mg/L, 0.5 mg/L, 0.25 mg/L and 0.1 mg/L. And then test the solution from low concentration in turn, taking the solution
concentration as the abscissa, the TOC value obtained from the test is plotted on the ordinate, and a standard curve Y is drawn. Accurately weigh 10 g of cement (accurate to 0.0001 g) and place it in a 100 mL beaker. Pour in accurately 80 mL of sample solution B. After stirring on a magnetic stirrer for 5 minutes, remove and place in a 30 °C water bath and let stand for 60 minutes. Take 50 mL of the upper suspension into a centrifuge tube. Centrifuge at 5000 r/min for 10 minutes, then take out and filter with a 0.45 μm filter to obtain solution C to be tested. The test solution C was used for the TOC test, the test injection volume was set to 0.25 mL. And the number of tests was 3 times. The TOC result measured by the test solution C is substituted into the standard curve Y to calculate the Water-reducing admixture concentration \( c_1 \) in the test solution C. Substitute the measured concentration of Water-reducing admixture \( c_1 \) into formula (1) to calculate the amount of Water-reducing admixture adsorbed in cement slurry \( r \).

\[
r = \frac{(c_1 \times V_1 - c_0 \times V_1)}{m \times 1000}
\]

In the formula: \( r \)-the amount of Water-reducing admixture adsorbed in the cement paste, mg/g. \( c_0 \)-Concentration of Water-reducing admixture sample solution, mg/L. \( V_1 \)-Volume of the sample solution added with Water-reducing admixture in the experiment, mL. \( c_1 \)-Concentration of Water-reducing admixture in test solution C, mg/L. \( m \)-cement weighs the sample mass, g.

Two commercially available Water-reducing admixture solutions, Water-reducing admixture A and Water-reducing admixture B, draw standard working curves as shown in Figure 1 and Figure 2 according to the test procedure described in Section C of Chapter II.

Figure 1. The standard working curves of Water-reducing admixture A

Figure 2. The standard working curves of Water-reducing admixture B
The test results in Figures 1 and 2 show that the linear relationship $r^2$ of the standard working curves of the two water reducers is greater than 0.999, indicating that the TOC content of the two types of water reducer solutions of different concentrations has a clear linear relationship with the solution concentration.

2.4 Selection of sample preparation conditions
This method conducted a comparative test on the stirring time, standing temperature and standing time in the pre-treatment conditions. The test results are shown in Figure 3 to Figure 5.

Figure 3. Effect of stirring time on adsorption

Figure 4. Effect of standing temperature on adsorption

Figure 5. Effect of standing time on adsorption
It can be seen from Fig. 3 that the amount of Water-reducing admixture adsorbed on the surface of cement particles increases first and then decreases with the increase of the stirring time. When the stirring time is 5 min, the amount of Water-reducing admixture adsorption reaches its maximum value. This may be because proper mixing is conducive to more fully dispersing the Water-reducing admixture on the surface of the cement particles. And the stirring time is too long, it will be detrimental to the adsorption of the dispersed Water-reducing admixture on the surface of the cement particles.

The experimental results in Figure 4 show that as the standing temperature increases, the amount of Water-reducing admixture adsorbed in the cement slurry first increases and then decreases rapidly. When the temperature is 30°C, the Water-reducing admixture has the best adsorption effect. This may be because when the temperature is low, increasing the temperature is beneficial to the dispersion of the Water-reducing admixture in the cement slurry, thereby promoting the adsorption of the Water-reducing admixture in the cement slurry, but too high a temperature will cause molecules in the cement slurry system too active, which is not conducive to the adhesion of Water-reducing admixture on the surface of cement particles.

The experimental results in Figure 5 show that the amount of Water-reducing admixture adsorbed on the surface of the cement particles increases with standing time and then tends to be stable. This may be because the concentration of Water-reducing admixture in the solution is large at the beginning, and the surface of the cement particles There is no Water-reducing admixture molecule, so the adsorption capacity increases rapidly with the standing time. After standing for a period of time, most of the Water-reducing admixture molecules have been adsorbed on the surface of the cement particles, and the concentration of the Water-reducing admixture in the solution The decrease and the space available on the surface of the cement particles for the analysis and adsorption of the water reducer become smaller.

3. RESULTS AND DISCUSSION

3.1 Accuracy experiment

The Water-reducing admixture B (containing 52.89% solids) was selected to prepare a 2.5mg/mL test solution 1 for accuracy experiments. The test results are shown in Table 2.

| Serial number | TOC (mg/L) | Sample measured concentration (mg/mL) | Actual concentration of sample (mg/mL) | Error (mg/mL) | Relative error (%) |
|---------------|------------|---------------------------------------|----------------------------------------|---------------|-------------------|
| Z-1           | 1367.314   | 2.5074                                |                                        | -0.0023       | 0.0009            |
| Z-2           | 1367.523   | 2.5077                                |                                        | -0.0020       | 0.0008            |
| Z-3           | 1370.315   | 2.5129                                |                                        | 0.0032        | 0.0013            |
| Z-4           | 1365.862   | 2.5047                                |                                        | -0.0050       | 0.0020            |
| Z-5           | 1369.720   | 2.5118                                |                                        | 0.0021        | 0.0008            |
| Z-6           | 1372.537   | 2.5171                                |                                        | 0.0074        | 0.0029            |
| Z-7           | 1370.152   | 2.5126                                |                                        | 0.0029        | 0.0012            |
| Z-8           | 1364.191   | 2.5015                                |                                        | -0.0082       | 0.0033            |
| Z-9           | 1371.314   | 2.5148                                |                                        | 0.0051        | 0.0020            |
| Z-10          | 1368.361   | 2.5093                                |                                        | -0.0004       | 0.0002            |

According to the experimental results, the relative error of 10 parallel experiments in this method is less than 0.005%, and the accuracy is well.
3.2 Repeatability evaluation

The test solution 1 prepared by the precision experiment shall be subjected to the repeatability test according to section c of Part II. The test results are shown in Table 3.

| Serial number | Cement (g) | Volume of additive solution (mL) | TOC (mg/L) | Γ (mg/g) | Average (mg/g) | RSD (%) |
|---------------|------------|----------------------------------|------------|----------|----------------|---------|
| J-1           | 10.0316    | 0.00                             | 64.69      | /        | /              | /       |
| J-2           | 10.0105    | 0.00                             | 63.27      | /        | /              | /       |
| J-3           | 10.0031    | 0.00                             | 63.76      | /        | /              | /       |
| J-4           | 10.0032    | 80.00                            | 318.62     | 16.0157  | 16.0543        | 0.6076  |
| J-5           | 10.0073    | 80.00                            | 306.83     | 16.1931  |                |         |
| J-6           | 10.0053    | 80.00                            | 315.37     | 16.0631  |                |         |
| J-7           | 10.0085    | 80.00                            | 312.05     | 16.1097  |                |         |
| J-8           | 10.0096    | 80.00                            | 308.63     | 16.1613  |                |         |
| J-9           | 10.0032    | 80.00                            | 321.54     | 15.9701  |                |         |
| J-10          | 10.0087    | 80.00                            | 318.52     | 16.0085  |                |         |
| J-11          | 10.0016    | 80.00                            | 309.66     | 16.1581  |                |         |
| J-12          | 10.0075    | 80.00                            | 324.38     | 15.9190  |                |         |
| J-13          | 10.0063    | 80.00                            | 322.86     | 15.9446  |                |         |

From the precision test results, the relative standard deviation (RSD) of the test results of the 10 parallel experiments is 0.6076%, the RSD value is smaller, and the test results show that the method has good repeatability.

4. CONCLUSION

A test method for the determination of the amount of Water-reducing admixture adsorbed on the surface of cement particles by the TOC method was established. The correlation coefficients of the standard curves of the Water-reducing admixtures were all greater than 0.999, and the relative error of the results of 10 parallel experiments of the method was less than 0.005%, the relative standard deviation (RSD) is 0.7706%.

Through the comparison test of the stirring time, standing time and standing temperature in the pre-treatment process, it is found that the best stirring time, standing time and standing temperature in the pre-treatment process of this method are: 5 min, 60 min and 30 °C. Using the Water-reducing admixture concentration and TOC concentration to make a standard curve can intuitively and accurately characterize the relationship between the Water-reducing admixture solution concentration and TCO, and then by measuring the remaining TOC in the solution after adsorption and the TOC value in the blank sample, the amount of water reducing admixture adsorbed on the surface of cement particles can be accurately calculated.

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