Sensitivity Evaluation Method of Polycarboxylate Superplasticizer on Aggregate Adsorption and Water Consumption

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Abstract: The dosage of polycarboxylate superplasticizer (PCE) is significantly affected by the content of sand and gravel aggregate mud powder and the fluctuation of water content. PCE with low sensitivity has better adaptability to raw materials. In order to evaluate the sensitivity of PCE, the methylene blue (MB) was used to characterize the adsorption capacity of manufactured sand, and the variation of PCE dosage with MB and water consumption was explored. Taking PCE-1 as an example, a mathematical model of the amount of PCE-1 changing with MB and water consumption was established. The adsorption coefficient a and the water consumption sensitivity coefficient w were used as the key parameters to evaluate the sensitivity of PCE. The lower the a, the lower the adsorption sensitivity of PCE, and the lower the w, the lower the water consumption sensitivity of PCE. The adsorption coefficients a of PCE-1 ~ PCE-4 were 1.1, 1.7, 1.7, 0.7, and the water consumption sensitivity coefficients w were 3.3, 4.0, 6.7, 5.0, respectively. Comprehensive comparison shows that PCE-1 has better adaptability to raw materials.

Keywords: Polycarboxylate Superplasticizer; Manufactured Sand; Adsorption; Sensitivity Evaluation

1. Preface

As one of the indispensable components of modern concrete, water reducing agent has experienced the first generation of ordinary water reducing agent represented by lignosulfonate, the second generation of high efficiency water reducing agent represented by nai system, and the third generation of high performance water reducing agent represented by polycarboxylic acid [1-3]. Polycarboxylate superplasticizer (PCE) has become the most widely used superplasticizer product in engineering projects and civil commercial mixing market due to its flexible slump retention timeliness and higher water reduction rate, durability, environmental protection and economic advantages in concrete. However, the amount of PCE is easily affected by the quality fluctuation of raw materials compared with the water reducer [4-6]. However, the concrete production volume of commercial and mixed enterprises is large, the raw material consumption is fast, and the water content of sand and gravel aggregate, the content of mud powder and other indicators are difficult to ensure stability, so higher requirements are put forward for the sensitivity of PCE [7-12].

At present, most civil commercial enterprises focus on the water reduction rate and slump retention performance of PCE, but lack of attention to the sensitivity of water reducing agent. When the quality of raw materials fluctuates, the production control of concrete is difficult, the fluidity of concrete is easy to increase when the water reducing agent is over mixed, the fluidity of concrete is easy to lose when the water reducing agent is under mixed, and the quality risk of concrete production is high [13]. In order to evaluate the sensitivity of water reducer to raw materials, the MB was used to characterize the adsorption capacity of manufactured sand, and the variation of PCE content at high and low MB and water consumption was explored. The mathematical model of the change of water reducer content with MB and water consumption of manufactured sand was established, which provided a reference for further evaluation of the adaptability of PCE to raw materials.

2. Test Overview

2.1 Raw Materials

A Cementitious materials: P • O 42.5 grade Fufeng Jidong cement, F • II grade Hancheng Huaneng fly ash, S95 grade Shanxi Witton slag, the main chemical composition of cementitious materials is shown in Table 1. Fine aggregate: the MB of manufactured sand.

A is 0.5, the MB of manufactured sand B is 2.5, and the particle gradation is shown in Table 2. Coarse aggregate: 5-25mm continuous grading gravel, particle gradation is shown in Table 3.

Water reducer: PCE-1, PCE-2, PCE-3, PCE-4 of Jiangsu Subote New Materials Co., Ltd.

Mixing water: laboratory tap water.

Table 1. Chemical Composition of Cementitious Materials

cementing material	SiO_2	CaO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3	miscellaneous
cement	23.20	54.91	7.55	3.74	0.42	1.58	0.37	2.79
flyash	40.06	22.87	17.24	7.32	1.56	1.23	2.30	5.26
mineral fines	30.10	40.48	12.63	0.52	0.65	8.52	0.65	3.31

Table 2. Particle Gradation of Manufactured Sand

sand	4.75	2.36	1.18	0.6	0.3	0.15	bottom	fineness modulus	MB
manufactured sand A	2	18	43	64	82	88	100	2.9	0.5
manufactured sand B	3	21	46	63	79	87	100	2.9	2.5

Table 3. Coarse Aggregate Particle Gradation

pebble	31.5	26.5	19.0	16.0	9.5	4.75	2.36	bottom
crushed stone	0	1	30	44	81	98	99	100
pebble	31.5	26.5	19.0	16.0	9.5	4.75	2.36	bottom

2.2 Test Method

The design grade of concrete is C30, the water-binder ratio is 0.47, and the sand ratio is 42 %. The test benchmark mix ratio is shown in Table 4. Firstly, the weighed gravel, manufactured sand and cementitious materials were put into the mixer for stirring for 30 s according to the feeding order, and then the mixing water and water reducer were added for stirring again for 2 min. When the initial expansion degree of concrete was 580 ± 10 mm, the amount of water reducer in this test was recorded.

Table 4. Benchmark Mix Ratio of Concrete (unit: kg/m3)

label	cement	flyash	mineral fines	sand	pebble	water
C30	200	80	60	790	1090	160

2.3 Sensitivity Evaluation

2.3.1 Sensitivity of PCE to adsorption capacity of manufactured sand

In order to evaluate the influence of the adsorption capacity of the manufactured sand on the sensitivity of the water reducer, the manufactured sand A and the manufactured sand B were combined according to the design ratio, so that the MB of the composite manufactured sand gradually increased from 0.7 to 2.3, as shown in Table 5. According to the dosage of water reducing agent in different MB environment, the influence law of MB on the dosage of water reducing agent is obtained, and the mathematical model of the influence of MB on the dosage of water reducing agent is established.

Table 5. Proportion of Composite Application of Manufactured Sand

number	manufactured sand A	manufactured sand B	composite ratio	complex sandMB
1-1#	711	79	9:1	0.7
1-2#	632	158	8:2	0.9
1-3#	553	237	7:3	1.1
1-4#	474	316	6:4	1.3
1-5#	395	395	5:5	1.5
1-6#	316	474	4:6	1.7
1-7#	237	553	3:7	1.9
1-8#	158	632	2:8	2.1
1-9#	79	711	1:9	2.3

2.3.2 Sensitivity of PCE to adsorption capacity and water consumption of manufactured sand

In order to evaluate the comprehensive influence of adsorption capacity and water consumption of manufactured sand on the sensitivity of water reducer content, two groups of MB and two groups of water consumption of manufactured sand were set, and a total of four groups of mixture ratios were set, as shown in Table 6. Among them, C30-1 is low adsorption capacity and low water consumption, C30-2 is low adsorption capacity and high water consumption, C30-3 is high adsorption capacity and low water consumption, C30-4 is high adsorption capacity and high water consumption. Using this mix design method, according to the amount of water reducing agent under four different MB and water consumption conditions, the variation law of the same water reducing agent product with MB and water consumption can be obtained, and the anti-adsorption sensitivity and water consumption sensitivity of the water reducing agent can be obtained. In addition, the sensitivity test results of different water reducers at the same mix ratio were compared, and the water reducer with the best adaptability was selected.

Table 6. C30 Concrete Mix Proportion (unit: kg/m3)

number	cement	flyash	mineral fines	manufactured sandA	manufactured sandB	pebble	water
2-1#	200	80	60	553	237	1090	160
2-2#	200	80	60	553	237	1090	170
2-3#	200	80	60	237	553	1090	160
2-4#	200	80	60	237	553	1090	170

3. Results and Analysis

3.1 Sensitivity of PCE to Adsorption Capacity of Manufactured Sand

When the initial expansion of concrete is 580 ± 10mm, the test results of the amount of water reducing agent with the change of composite sand MB are shown in Table 7. It can be seen from Table 7 that the amount of water reducing agent is significantly affected by the change of MB, and the amount of water reducing agent increases with the increase of MB. When MB is 0.7, the dosage of water reducing agent is 2.1 %, and the dosage is 7.14 kg / m3. When MB is 2.3, the dosage of water reducing agent is 4.0 %, the dosage of water reducing agent is 13.6 kg / m3, the dosage of water reducing agent is increased by 1.9 times, and the dosage of water reducing agent of single concrete is increased by 6.64 kg. When MB increased from 0.9,1.1 to 2.2, the amount of water reducer increased by 1.05 times, 1.19 times to 1.71 times, respectively, indicating that the amount of water reducer increased linearly with the change trend of MB.

Table 7. The Test Results of the Influence of Manufactured Sand MB on the Amount of Water Reducing Agent

number	complex sand MB	water / %	dosage of water reducing agent kg/ m^3	initial expansion / mm
1-1#	0.7	2.1	7.1	575
1-2#	0.9	2.2	7.5	580
1-3#	1.1	2.5	8.5	580
1-4#	1.3	2.7	9.2	585
1-5#	1.5	3.0	10.2	580
1-6#	1.7	3.2	10.9	580
1-7#	1.9	3.4	11.6	580
1-8#	2.1	3.6	12.2	585
1-9#	2.3	4.0	13.6	590

The test results are mathematically fitted to obtain y = a • x + b, where y is the amount of water reducing agent, x is MB, a = 1.175, b = 1.2042, and the correlation coefficient R2 = 0.9921, indicating that the amount of water reducing agent changes with MB. The linear regularity is strong, as shown in Figure 1. In the above formula, a is the slope of the change of the amount of water reducer with MB, which reflects the adsorption capacity of the mechanism sand to the water reducer. The smaller the value of a, the smaller the influence of the mechanism sand MB on the amount of water reducer, indicating that the water reducer has stronger anti-adsorption capacity. b is the amount of water reducing agent when MB is 0, which reflects the basic amount of water reducing agent. The larger the b value is, the greater the basic adsorption capacity of raw materials to water or admixture is.

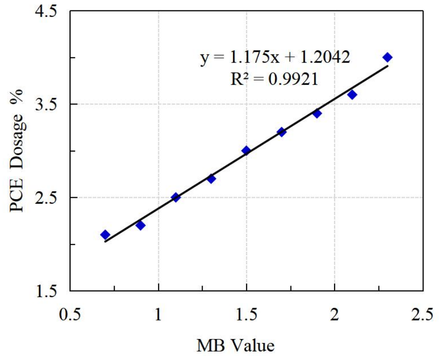

Figure 1. The Influence of MB Change on the Dosage of Water Reducing Agent

3.2 Sensitivity of PCE to Adsorption Capacity and Water Consumption of Manufactured Sand

When the initial expansion of concrete is 580 ± 10mm, the test results of the amount of water reducing agent with the change of composite sand MB are shown in Table 8. It can be seen from Table 8 that for the same water reducer, the amount of water reducer is different under different MB and water consumption conditions. MB and water consumption have different effects on the amount of water reducer. Increasing MB increases the amount of water reducer, and increasing water consumption reduces the amount of water reducer. By comparing 2-1 and 2-2, it can be seen that when MB is 1.1, water consumption is 160 kg / m3 and 170 kg / m3, the dosage of water reducing agent is 2.5 % and 2.2 % respectively, and 10 kg water consumption can be reduced by 0.3 %. When MB is 1.1, 0.1 % dosage corresponds to 3.3 kg water consumption ;By comparing 2-3 and 2-4, it can be seen that when MB is 1.9, water consumption is 160 kg / m3 and 170 kg / m3, the dosage of water reducing agent is 3.4 % and 3.1 % respectively, and 10 kg water consumption can also be reduced by 0.3 %, indicating that PCE-1 has the same sensitivity to water consumption when MB is 1.1 and 1.9, and the water consumption corresponding to 0.1 % dosage is 3.3 kg ; comparing 2-1 and 2-3, it can be seen that when the water consumption is 160 kg / m3, MB is 1.1 and 1.9, the dosage of water reducer is 2.5 % and 3.4 %, respectively. The increase of MB by 0.8 leads to an increase of 0.9 %, indicating that when the water consumption is 160, the 0.1 % dosage can adapt to the change of MB by 0.09. Comparing 2-2 and 2-4, it can be seen that when the water consumption is 170 kg / m3, MB is 1.1 and 1.9, the dosage of water reducer is 2.2 % and 3.1 % respectively, indicating that when the water consumption is 160 kg / m3 and 170 kg / m3, MB has the same effect on the dosage.

Table 8. Experimental Results of the Influence of MB and Water Consumption on the Dosage of Water Reducer

number	complex sand MB	water / kg	water reducing agent dosage / %	dosage of water reducing agent kg/ m^3	initial expansion / mm
2-1#	1.1	160	2.5	8.5	580
2-2#	1.1	170	2.2	7.5	585
2-3#	1.9	160	3.4	11.6	580
2-4#	1.9	170	3.1	10.6	575

3.3 Mathematical Model of PCE Sensitivity Evaluation of Manufactured Sand

The test results of the amount of water reducing agent with MB under different water consumption were mathematically fitted, and y = a • x + b was obtained. When the water consumption was 160, a = 1.125, b1 = 1.2625, when the water consumption was 170, a = 1.125, b2 = 0.9625. From the previous section, it can be seen that the parameter a reflects the adsorption capacity of the manufactured sand to the water reducing agent. The smaller the parameter a, the weaker the adsorption capacity of the manufactured sand to the water reducing agent, which represents the stronger the anti-adsorption capacity of the water reducing agent. The sensitivity coefficient w = 1 / (b1-b2) of water consumption for every 0.1 % change in the dosage of water reducer is defined. In this experiment, the w = 3.3 of PCE-1 indicates that the greater the w, the higher the sensitivity of water reducer to water consumption.

The calculation results of adsorption coefficient a and water consumption sensitivity coefficient w of PCE-2, PCE-3 and PCE-4 were obtained by the same test method, as shown in Table 9. By comparing the adsorption coefficient a, it is concluded that the value of PCE-4 is the smallest, indicating that the adsorption amount of PCE-4 by the manufactured sand is the least, and the anti-adsorption ability of PCE-4 is the strongest, followed by the anti-adsorption ability of PCE-1 is weak, and the anti-adsorption ability of PCE-2 and PCE-3 is the weakest. Comparing the water consumption sensitivity coefficient w, it is concluded that the water consumption sensitivity of PCE-1 is the lowest, indicating that the change of PCE-1 content is the smallest when the water consumption changes. Secondly, the water consumption sensitivity of PCE-2 and PCE-4 is higher. PCE-3 has the highest sensitivity to water consumption. When the water reducer is selected in practical application, its anti-adsorption capacity and water consumption sensitivity should be taken into account. For the above four water reducers, PCE-1 has the best adaptability.

Table 9. Calculation Results of Adsorption Coefficient a and Water Consumption Sensitivity Coefficient w of Water Reducing Agent

	PCE-1	PCE-2	PCE-3	PCE-4
adsorption coefficienta	1.1	1.7	1.7	0.7
Water consumption sensitivity coefficientw	3.3	4.0	6.7	5.0

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5. Conclusion

In this paper, the anti-adsorption and sensitivity to water consumption of polycarboxylate superplasticizer were evaluated by using four kinds of mixture ratios: low adsorption and low water consumption, low adsorption and high water consumption, high adsorption and low water consumption and high adsorption and high water consumption. The main results are as follows:

1) The amount of water reducing agent increases linearly with the increase of MB in a certain range.

2) The adsorption coefficient a reflects the anti-adsorption of water reducer by manufactured sand. The smaller the a is, the less the water reducer adsorbed by manufactured sand is, and the stronger the anti-adsorption ability of water reducer is.

3) The water consumption sensitivity coefficient w reflects the sensitivity of water reducing agent to water consumption. The greater the w, the greater the influence of water consumption change on the dosage of water reducing agent, and the higher the sensitivity of water reducing agent to water consumption.

Combined with the adsorption coefficient a and the water consumption sensitivity coefficient w, the anti-adsorption capacity and water consumption sensitivity of different polycarboxylate superplasticizers to raw materials can be compared, so as to make a more comprehensive evaluation of the adaptability of superplasticizers to raw materials.

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