Experimental Study on Modification of Low-grade and Machine-made Sands

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Abstract: In order to better apply low-grade and machine-made sands, this paper adopts the control test to investigate the influence of low-grade and machine-made sands with different proportions on motor fluidity, setting time and compressive strength, and modification effects of different mud inhibitors on low-grade and machine-made sands, proceeds the study on suitability of different kinds of fine low-grade and machine-made sands, and conducts the scale-up experiment in the concrete. The research results show that the content of fine low-grade and machine-made sands can substantially influence the water-reducing effects of polycarboxylate superplasticizer, affect the motor fluidity, compressive strength and setting time. After comparing different kinds of mud inhibitors, it turns out that HEDP has better effects, and can improve the low-grade and machine-made sands to certain degree; after comparing the polyethylene glycol (PEG) with different molecular weights, it turns out that the less the molecular weight is, the better the mud resistance effects are; PAANa has the best effects, and can remarkably improve the motor fluidity, prolong the setting time, enhance the compressive strength, and has better adaptability to different kinds of low-grade and machine-made sands, same significant application effects in concrete.

1. Introduction

The rapid development of the construction industry stimulates the increase in demand of concrete, sands and gravel aggregates. According to the relevant data statistics, the annual demand of sands and gravel aggregates is approximately 20 billion ton. Due to the restrictions on mining river sands imposed by Chinese Government, the proportion of low-grade and machine-made sands in the market has been increasing, with relatively high content in mud and stone powder, and poor gradation, and all these factors will undermine the construction quality and long-term compressive strength[1]. In order to meet requirements for the workability of concrete during the use process, the proportion of admixtures has been remarkably increased, thus substantially escalating the production cost[2-4]. The polycarboxylate superplasticizer used in vast quantities in the production, due to the combination of multiple advantages, has a promising application prospects. However, it is especially sensitive to the mud content in the aggregates[5]. Since clay, the main component of soil particles, has unique interlayered structure, while the side chain in the comb-type molecular structure of polycarboxylate superplasticizer is generally long and thin. Wang Lin et al[6-7] proves that the side chain of
The polycarboxylate superplasticizer can be easily absorbed to the inter-layers of clay minerals via XRD test, and as a result, the whole polycarboxylate molecules will be firmly anchored to the clay particles, thus jeopardizing the dispersing power\cite{8-10}. Engineering qualitative accidents caused by failure of polycarboxylate superplasticizer due to the exceeding content of mud is not uncommon, but the method to reduce the mud content by water washing, due to the complex technology, will not only boost the cost in human and material resources, but also result in the sewage discharge and sludge. Therefore, developing a low-cost modifying agent for the low-grade and machine-made sands has become more imperative.

According to the study of Fang Xin et al, when adding polycarboxylate superplasticizer to the concrete, if the mud content in the sands is more than 5\%, the polycarboxylate superplasticizer will almost become invalid after about 1h\cite{11}; Bian Rongjun points out in his paper that acrylic acid hydroxyalkyl ester, as a kind of mud inhibitor, can effectively reduce the sensitivity of polycarboxylate superplasticizer to mud\cite{12}; Liu Guodong et al proceeds the liquid-plastic limit test on the soil to adjust the proportion of polycarboxylate superplasticizer and mud inhibitor in order to reduce the dose of polycarboxylate superplasticizer and improve the concrete properties\cite{13}; Zang Jun et al control the dispersing power and swelling of clay by adding inorganic potassium salt and clay stabilizers, and combine the organophosphorus scale inhibitor to inhabit the direction contact between polycarboxylate superplasticizer and clay in order to achieve the purpose of sustaining the water-reducing effects of polycarboxylate superplasticizer\cite{14}.

Till now, there is little research on the influence of the content of fine low-grade and machine-made sands and different kinds of mud inhibitors on mortar fluidity, setting time and compressive strength at different ages. This paper tests and observes the influence of low-grade and machine-made sands with different proportions on all kinds of mortar properties, compares the inhibiting effects of different mud inhibitors, and proceeds the verification test on the adaptability of mud inhibitors to different fine low-grade and machine-made sands, and conducts the scale-up experiment in the concrete. These results can serve as the reference for the application of low-grade and machine-made sands.

2. Test

2.1. Raw materials

Cementing materials: ordinary portland cement P. O 42.5 (from a factory in Jinan), with its chemical composition as shown in Table 1.

|          | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | R₂O | Loss on ignition |
|----------|------|-------|-------|-----|-----|-----|-----|-----------------|
|          | 23.75| 4.35  | 3.35  | 59.55| 2.55| 3.05| 0.60 | 0.80            |

Aggregates: 20-40 mesh quartz sands available in the market; 40-70 mesh quartz sands available in the market; 70-120 mesh quartz sands available in the market; low-grade and machine-made sands from a factory in Jinan, with the methylene blue (MB) value being 1.2.

Mineral admixtures: ultra-fine mineral powder (from a factory in Jinan), Type I fly ash, commercially available. The chemical composition of fly ash and mineral power is as shown in Table 2.

|          | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SO₃ | R₂O |
|----------|------|-------|-------|-----|-----|-----|-----|
| Superfine mineral powder | 35.23 | 10.16 | 0.94 | 10.25 | 5.04 | 0.15 |
| Fly ash | 18.30 | 27.32 | 8.40 | 0.25 | 0.95 | 0.52 |

Admixture: polycarboxylate superplasticizer PC-XM (from Shandong Huadi Architectural Technology Co., Ltd.), pumping aid (from Shandong Huadi Architectural Technology Co., Ltd.), all kinds of mud inhibitors: HEDP (from Changzhou Runyang Chemical Co., Ltd.), CTAC (from
Shandong Yousuo Chemical Technology Co., Ltd.), PEG-200 (from Wuxi Yatai Allied Chemical Co., Ltd.), PEG-600 (from Wuxi Yatai Allied Chemical Co., Ltd.), PEG-1000 (from Wuxi Yatai Allied Chemical Co., Ltd.), sodium gluconate (from Weifang Jianbao Biotechnology Co., Ltd.), PAANa (homemade).

Water: tap water.

2.2. Test instruments, equipment and models

Test instruments and equipment are as shown in Table 3.

Table 3. Instrument and equipment for testing

| Equipment name                        | Number | Model     | Purpose                        |
|---------------------------------------|--------|-----------|--------------------------------|
| Mortar setting time tester            | 1      | ZSK-100   | Measurement of setting time    |
| Standard constant temperature and humidity curing box | 1  | YH-40B   | Curing test block              |
| Cement mortar mixer                   | 1      | JJ-5      | Mortar mixing                  |
| Pressure tester                       | 1      | TYE-300B  | Compression test of test block |
| Model test                            | 24     | 70.7mm×70.7mm×70.7mm | Paste forming          |
| balance                               | 6      | 15cm×15cm×15cm | Weighing of raw materials    |

2.3. Test design

- Replace the fine aggregates in Table 4 (20-40 mesh quartz sands, 40-70 mesh quartz sands and 70-120 mesh quartz sands) with stone powder and soil with the diameter less than 75 μm sieved from low-grade and machine-made sands with different mixing proportions (2%, 4%, 6%, 8% and 10%) and then well-proportioned (fine low-grade and machine-made sands DSF). Purpose: study the effect of DSF with different proportions on mortar fluidity, setting time and compressive strength.

The low-grade and machine-made sands adopted in this test come from one factory in Jinan. By referring to the quantitative analysis method marked by methylene blue proposed by Wu Jinzao et al [15], this paper tests the stone power and soil content in the used low-grade and machine-made sands, and it turns out that particles with the diameter less than 75 μm in this machine-made sands consist of 60% stone power and 40% clay.

Table 4. Mortar mix proportion(g)

| Cement powder | Fly ash | 20-40 mesh Quartz sand | 40-70 mesh Quartz sand | 70-120 mesh Quartz sand | Water | admixture (PC-XM) |
|---------------|---------|------------------------|------------------------|------------------------|-------|-------------------|
| 240           | 80      | 80                     | 200                    | 300                    | 300   | 150               | X               |

- Replace 10% fine aggregates in Table 4 with DSF (replace 10% of 20-40 mesh quartz sands, 10% of 40-70 mesh quartz sands and 10% of 70-120 mesh quartz sands with DSF), add different kinds of mud inhibitors (including HEDP, PAANa, sodium gluconate, CTAC, PEG-200, PEG-600 and PEG-1000) at the dose of 0.3g respectively into the mix proportion shown in Table 4, compare them with the blank samples (PC-XM) to get the modification effects of different mud inhibitors on DSF, observe the fluidity and setting time, compare the compressive strength on the 3rd day, the 7th day and 28th day, and find out the mud inhibitor with the best modification effects on low-grade and machine-made sands.

- Verify the adaptability of the mud inhibitor with the best modification effects on different fine low-grade sand power.

- Verify the effect of the mud inhibitor with the best modification effects in the concrete.
3. Test Results and Discussion

3.1. Effects of mud content on all mortar properties
Carry out the experimental study by DSF-free control groups and adding DSF with different proportions under the condition with same proportion of admixture, with the test results as shown in Figure 1(a). Add the dose of polycarboxylate superplasticizer to achieve the approximate initial fluidity under the condition with different dose of DSF, and compare it with the control groups to obtain the fluidity loss as shown in Figure 1(b), setting time (Figure 2) and compressive strength (Figure 3).

![Figure 1. Effect of DSF content on initial fluidity and time-lapse of fluidity of mortar](image)

As shown in Figure 1, along with the increase of DSF proportion, the initial fluidity of mortar decreases gradually, and when the DSF proportion increases to 8%, the initial fluidity has lost, which clearly proves that DSF content will substantially jeopardize the initial fluidity of mortar. Under the condition of controlling the initial fluidity at the same level, along with the increase of DSF proportion, the loss of long-term fluidity will markedly increase. When the DSF proportion increases to 8%, the fluidity will decline by half after 30min, and completely lose after 60min; when the DSF proportion increases to 10%, the fluidity of mortar will completely lose at the moment of 30min, failing to meet the project demands. The influence of DSF on the fluidity of mortar can be attributed to the strong absorption of special inter-layered structure of soil to polycarboxylate superplasticizer, thus jeopardizing the dispersing power of polycarboxylate molecules; meanwhile, the large specific surface area of soils can absorb large amount of free water, thus making the mortar more sticky and liquidity worse. In addition, there will be vast amount of Si-O broken bonds on the surface of stone powder during the process of crushing sand and gravel aggregates, which will change the systematic charge distribution; at the same time, there may also be planar defects, which can enhance the absorption of DSF and lead to the severe loss of the fluidity of mortar.

As shown in Figure 2, when the DSF content increases, the measure to meet the proper initial fluidity by adding the dose of polycarboxylate superplasticizer has little impact on the mortar’s setting time, with the initial setting time of DSF with different proportions varying no more than 1h, and final setting time no more than 1h. Since along with the increase of DSF, the mud content will increase, and due to the strong absorption of soils to polycarboxylate superplasticizer, the fluidity loss of mortar will speed up, the setting time will get shortened. However, the increase of dose of polycarboxylate superplasticizer will accordingly prolong the setting time of mortar. The mutual offset of these two effects will not affect the hydration reaction process of mortar, in this way, the setting time will not vary a lot.
As shown in Figure 3, when the DSF proportion is no more than 2%, the compressive strength at different ages will slightly increase, since the adding of DSF will increase the fine aggregates in the mortar, and then enhance the density. Along with the continuous increase of DSF proportion, the compressive strength at the early stage and the long-term compressive strength will gradually decline. When DSF increases from 2% to 10%, the compressive strength on the 3rd day will decline from 21.8 MPa to 18.3 MPa, with a decline of 16.0%; the compressive strength on the 7th day will decline from 33.2 MPa to 28 MPa, with a decline of 15.7%; the compressive strength on the 28th day will decline from 43.9 MPa to 36.5 MPa, with a decline of 16.9%. When the DSF proportion is more than 2% and increase gradually, the gradation of mortar declines, the density will get weakened, at the same time, the bonding power between C-S-H gels and between gels and aggregates will also be affected. Furthermore, the soil in the DSF will easily appear in the form of mud pies in the mud slurry to form the structural weak area, thus resulting in certain quality defects in the hardened test blocks. This can be the reason why the compressive strength of mortar declines.

3.2. Comparison on the effects of mud inhibitors
Replace 10% fine aggregates in Table 4 with DSF, respectively add different kinds of mud inhibitors with the dose of 0.3g (effective constituent) to carry out the test, compare them with the blank sample, compare the inhibiting effect, observe the fluidity (shown in Figure 4), setting time (Figure 6) and compressive strength (Figure 7). Types and number of mud inhibitors are as shown in Figure 5.

As shown in Figure 4, PAANa (as shown in Figure 5b), HEDP, PEG and sodium gluconate have certain modification effects on DSF. Under the condition without adding mud inhibitors, the mortar has no fluidity at the very beginning as shown in Figure 5(a), while the adding of mud inhibitors will markedly improve the fluidity, with the initial fluidity larger than that of bank sample, and the fluidity loss declining to a certain degree after 30min. For all PEGs, PEG-200 has the best effect, while PEG-1000 the worst effect. For the test group with CTAC added, it has evident air entraining effect, but has no distinct improvement in the fluidity, with the fluidity completely losing after 30min. Over time, the inhibiting effect of PEG and sodium gluconate will gradually wear off, while the inhibiting effect of PAANa and HEDP still remain distinct. Especially for PAANa, it can still remain excellent fluidity after 60min. This is because before the soils absorb polycarboxylate superplasticizer, PAANa will firstly fill up the inter-layered structure of soils, in which way the strong absorption effect of soils on water reducing agents will be inhibited and the water-reducing effect of polycarboxylate superplasticizer will be effectively achieved.
Table 5. Types and numbers of mud inhibitors

| Number | Name of mud inhibitor                  |
|--------|---------------------------------------|
| 1      | Blank sample                          |
| 2      | Polyethylene glycol 200               |
| 3      | Polyethylene glycol 600               |
| 4      | Polyethylene glycol 1000              |
| 5      | Cetyltrimethyl ammonium chloride      |
| 6      | PAANa                                 |
| 7      | HEDP                                  |
| 8      | Sodium gluconate powder               |

Figure 4. Fluidity of mortar under different mud inhibitors

As shown in Figure 6, sodium gluconate powder, HEDP and PAANa have distinct long-setting effects, with the initial setting time and final setting time improved by more than 2h. In this way, they can not only effectively address the problem of short setting time caused by soils, but also have remarkable effect in prolonging the setting time. However, other mud inhibitors have little impact on the setting time.
As shown in Figure 7, all kinds of mud inhibitors have little overall impact effect on the compressive strength of mortar. Special attention has been paid to the compressive strength of mortar after adding PAANa and HEDP with relatively good inhibiting effects, when compared with the blank control group, the compressive strength of the group added with PAANa increases by 3.4 MPa on the 3rd day, 5.7 MPa on the 7th day, and 6.2 MPa on the 28th day; the compressive strength of the group added with HEDP does not vary a lot at different ages, with the decline of 0.4 MPa on the 3rd day, with the increase of 4 MPa on the 7th day, and with the decline of 1.4 MPa on the 28th day.

After summing up the above-mentioned test data and conducting corresponding analysis, among the above-mentioned mud inhibitors, the mud inhibitor with the best inhibiting effect is PAANa. With acrylic acid as the unsaturated monomer, the sodium methallyl sulfonate as the chain transfer agent, and the introduction of cationic monomer, PAANa will become amphoteric small-molecule modifier synthesized by free radical polymerization. The group added with PAANa is featured with the best fluidity of mortar, and the compressive strength of mortar at different ages has been enhanced to a certain degree, with the maximum improvement in the compressive strength. It also possesses certain long-setting effects, which can effectively solve all kinds of problems related to mortar properties caused by soils.

### 3.3. Verification on the adaptability of mud inhibitors

Considering the potential selectivity of PAANa, a kind of mud inhibitor, on different fine low-grade and machine-made sands, replace 5% of fine aggregates in Table 4 with the fine low-grade and machine-made sands produced in Hubei, and compare the blank sample and the group adding PAANa with the best inhibiting effects; moreover, replace 5% of fine aggregates in Table 4 with the fine low-grade and machine-made sands produced in Sichuan, and compare the blank sample and the group adding PAANa with the best inhibiting effects, with the test results as shown in Table 6.

| Types of manufactured sand | Fluidity/mm | Setting time/h | Compressive strength/MPa |
|---------------------------|-------------|----------------|--------------------------|
|                           | initial     | 30min          | 1h                       | Initial setting | Final coagulation | 3d | 7d | 28d |
| Manufactured sand in Hubei Province Blank sample | 240 | 180 | 140 | 3 | 4 | 19 | 28 | 39 |
| PAANa | 255 | 210 | 185 | 4.2 | 5.5 | 22 | 32 | 43 |
| Blank sample | 245 | 190 | 145 | 2.8 | 4.1 | 20 | 31 | 42 |

### Table 6. performance comparison of mortar
The results of these two groups of control test show that PAANa has excellent adaptability in different DSF fine powders. The group adding PAANa has better effects on the setting time, compressive strength and fluidity of mortar, namely, the initial fluidity of this group is slightly improved than that of blank sample, the fluidity loss declines remarkably, the setting time has been prolonged, and the compressive strength on the 3rd day, the 7th day and the 28th day has been enhanced to a certain degree. This means that PAANa has good adaptability to different DSF, and can perfectly address the engineering problems caused by mud contained in the machine-made sands.

### 3.4. Concrete test

Follow the mix proportion of C40 concrete (as shown in Table 7), compare the blank sample (pumping aid: NF-2) and the control group adding PAANa, and test the inhibiting effects of PAANa in concrete.

| Project | Blank sample | PAANa |
|---------|--------------|-------|
| Slump/mm | Initial: 230 | 240 |
| 30min | 180 | 230 |
| 1h | 150 | 200 |
| Expansion/mm | Initial: 560 | 600 |
| 30min | 400 | 540 |
| 1h | 320 | 480 |
| Compressive strength (MPa) | 3d: 24 | 25 |
| 7d: 32 | 35 |
| 28d: 44 | 48 |

Test results show that the workability of mixture of C40 concrete adding PAANa has been remarkably improved, the gradual loss in slump and flow significantly decreases when compared with the control group without adding PAANa, the cube compressive strength at different ages has been enhanced to a certain extent. In conclusion, PAANa has prominent inhibiting effects in concrete.

### 4. Conclusion

- The content of fine low-grade and machine-made sands will not only affect the initial fluidity of mortar, but also substantially jeopardize the gradual loss of the fluidity of mortar. In the high-grade DSF system, controlling the initial fluidity by simply adding the dose of polycarboxylate superplasticizer is impossible to meet the production demands. In addition, when the DSF proportion is no more than 2%, the compressive strength of mortar will be enhanced, and when the DSF proportion is more than 2%, the compressive strength will gradually decrease along with the increase of DSF.

- PEGs have general inhibiting effects, and have no distinct improvement in all mortar properties. But the smaller the molecular weight is, the better the inhibiting effects are. In terms of improving the fluidity, PEG-200 has the best effect, but has no obvious improvement effects in the compressive strength of mortar, while PEG-1000 has the worst effect.

- CTAC has clear air entraining effects, but has no obvious improvement in the fluidity, with the compressive strength declined.

- Sodium gluconate powder, HEDP and PAANa have distinct long-setting effects, and can perfectly address the problem of short setting time caused by soils.
PAANa has the best modification effect on DSF. Adding PAANa can not only perfectly improve the fluidity of mortar, prolong the setting time, but also enhance the compressive strength, with the same distinct effects in the concrete. It can effectively solve the engineering problems caused by exceeding mud content and powder content in the low-grade and machine-made sands. HEDP can achieve better modification effects, and significantly improve the fluidity of mortar.

Reference
[1] Wang.G.F., Ma, J.W., Zhang.T., (2011) Influence of mud content on concrete with polycarboxylate superplasticizer and measures. J. China Building Materials Science and technology.; 3-5.
[2] Yang.Z.D., Cai.S.Q., Qin.S., et al. (2004) Study and application of integral anti swelling water injection technology in low permeability and strong water sensitive reservoir. J. Special oil and gas reservoir, 11: 86-88.
[3] Xi.P., Hu.X.Q, Zhao.D.B, et al. (1996) Synthesis of epichlorohydrin dimethylamine cationic polymer. J. Journal of polymer materials science and engineering, 12: 50-54.
[4] Joo.D.J., Shin.W.S., Kim.Y.H., (2008) Effect of Polyamine Flocculant Types on Dye Wastewater Treatment. J. Speration Science and Technology, 38: 661-678.
[5] Shang.Y.G., (2009) Synthesis and anti swelling performance evaluation of quaternary ammonium salt clay stabilizer. D. Ocean University of China.
[6] Wang L., (2014) Effect and mechanism of clay minerals on properties of polycarboxylate superplasticizer. D. Beijing: Tsinghua University.
[7] Plank J, Keller H, Andres P R, et al. (2006) Novel organo-mineral phases obtained by intercalation of maleic anhydride–allyl ether copolymers into layered calcium aluminum hydrates. J. Inorganica Chimica Acta, 59: 4901-4908.
[8] Ye.R.R, Wang.H., Wang.Q.B., et al. (2015) Review on the influence of clay on the dispersibility of polycarboxylate superplasticizer. J. Commercial concrete: 30-33.
[9] Huang.T.Y., Wang.D.M., Hou.Y.F., et al. (2014) Influence of clay and limestone powder on properties of cement paste. J. Concrete: 76-84.
[10] Yang.Y., Ran.Q.P., Mao.Y.L., (2012) Adsorption behavior of polycarboxylate superplasticizer on montmorillonite. J. Acta building materials, 15: 464-468.
[11] Fang.Xin, Wei.P, Zeng.C.M., (2015) Effect of aggregate mud content on polycarboxylate superplasticizer and treatment methods. J. Jiangxi building materials: 10-10.
[12] Bian.R.J., (2014) Research progress and current situation of concrete admixtures. N. China building materials news.
[13] Liu.G.D, Guan.Z.M., Wei.C.T., et al. (2008) Influence of sand mud content on properties of concrete mixed with polycarboxylate superplasticizer and effective countermeasures. J. Commercial concrete, 15-18.
[14] Zang.J., Zhao.C.J., Ji.X.K., (2013) A method to solve the poor adaptability of polycarboxylate and high mud content aggregate. J. Commercial concrete: 33-34.
[15] Wu.J.Z., Zhong.S.H., Wang.S.Y., et al. (2007) Exploration of detection method of mud content in artificial sand. J. Water conservancy and hydropower construction: 73-75.