Effect of superplasticizer and silica fume on the properties of self-compacting mortars

A O Smirnov¹, L M Dobshits² and S N Anisimov¹

¹Department of Building Technologies and Automobile Roads, Volga State University of Technology, 3 Lenin Square, Yoshkar-Ola 424000, Russia
²Department of Building Materials and Technologies, Russian University of Transport (MIIT), 9 b 9 Obrazcova Street, Moscow 127994, Russia

E-mail: smiralex93@gmail.com

Abstract. Self-compacting concrete is a highly flowing concrete that compact under self-weight without any vibration effort. The mortar phase of self-compacting concrete determines its rheological, strength characteristics, and durability. This paper discusses the effect of superplasticizer and silica fume on the properties of self-compacting mortars. Mini-slump flow diameter tests were conducted to determine the rheological properties of mortar mixtures, and compressive strength, density, water absorption, porosity experiments to assess the hardened properties of mortar specimens. Analysis of regression models shows that the use of superplasticizer reduces the water demand of mortar mixtures by up to 40 %, and the addition of silica fume leads to the densification of cement stone structure and reduces the porosity of concrete to 24 %. The maximum compressive strength at 2 days can be achieved with a superplasticizer content of 0.8-1.0 % and 0-5 % silica fume by binder weight, and at 28 days – with 1.0-1.2 % superplasticizer and 10-15 % silica fume content. According to X-ray phase analysis in a cement stone containing superplasticizer and silica fume, the degree of cement hydration increases and reduces the amount of portlandite, which leads to an increase in the strength and durability of the concrete.

1. Introduction

Self-compacting concrete is one of the most significant developments in concrete technology. It is a highly flowing concrete that compact under self-weight without any vibration effort [1–5]. Obtaining a new type of concrete has become possible thanks to the use of modern polycarboxylate superplasticizers. These superplasticizers provide high workability of concrete mixtures, increase the density of cement paste by reducing the water-cement ratio, and removing entrained air during self-compaction [6–8]. However, the use of superplasticizers does not provide sufficient expansion of aggregate grains, in which the concrete mixture will be resistant to segregation. Reducing bleeding and segregation of self-compacting concrete mixture is achieved by increasing the cement consumption [9]. For this reason, one of the disadvantages of self-compacting concrete is its high cost. High cement content also leads to increased hydration heat and shrinkage of concrete [10].

By replacing part of the cement with mineral additives, the cost of self-compacting concrete can be significantly reduced, especially if the mineral additives are waste or by-products of industry [11,12]. Such mineral additives as fly ash, blast furnace slag, and silica fume are widely used in self-
compacting concrete [13,14]. These mineral additives not only improve the homogeneity and workability of concrete mixtures but also can increase the strength and durability of concrete [15,16].

One of the methods of self-compacting concrete mix design is to study the properties of self-compacting mortars. The mortar phase of the mixture provides the expansion of coarse aggregate grains and determines the rheological, strength characteristics, and durability of self-compacting concrete [17–20]. At the same time, determining the rheological characteristics of self-compacting mortars is more precisely and less labor-consuming. Therefore, the influence of modifying admixtures on the properties of self-compacting concrete was studied on their mortar phase.

The purpose of this paper was to study the effect of superplasticizer and silica fume on the properties of self-compacting mortars, as well as to determine the optimal dosages of admixtures in the organomineral modifier composition for producing self-compacting concretes.

2. Materials and methods

The influence of superplasticizer and silica fume was studied on self-compacting mortar mixtures with a cement-sand ratio 1:2. For the preparation of the mixtures, Portland cement CEM I 52.5 N manufactured by LLC «South Ural Mining Processing Company» was used in work. The clinker of this cement had the following mineralogical composition: C3S – 62.6 %; C2S – 12.7 %; C3A – 4.6 %; C4AF – 13.5 %. Local fine-grained quartz sand with a fineness modulus of 1.76 and particle size distribution (0-0.315 mm – 40 %, 0.315-0.63 mm – 46 %, 0.63-1.25 mm – 11 %, 1.25-2.5 mm – 3 %) was used as an aggregate. Ferroalloy industry by-product, silica fume MK-85 produced by PJSC “Novolipetsk Metallurgical Plant” with a bulk density of 175 kg/m3 and mass content of silicon oxide SiO2 of 92 % was used as an active mineral additive. To ensure the necessary rheological properties of mortar mixtures, Sika ViscoCrete 25 HE-C polycarboxylate superplasticizer was used in the study.

A two-factor experiment was planned to study the patterns of cement systems structure formation in the modifying admixtures presence and determine their optimal dosages in the organomineral modifier composition.

The content of superplasticizer and silica fume varied within the following limits:

- X1 – the amount of Sika ViscoCrete 25 HE-C superplasticizer, in percentage by binder weight – from 0.4 % to 1.2 %.
- X2 – the amount of MK-85 silica fume, in percentage by binder weight, added instead of cement – from 5 % to 15 %.

Control not containing silica fume compositions were also investigated to refine the model.

The water-binder ratio of mortar mixtures (W/B), the fine-grained concrete strength at 2, 7, and 28 days (R2, R7, R28), the density (ρ), and open capillary porosity (Po) of the samples were considered as responses from a two-factor experiment.

The amount of mixing water in the compositions was selected from the conditions for obtaining self-compacting mixtures with the same workability. The workability of mortar mixtures was estimated by the flow spread diameter of cement-sand mortars from the Hagerman’s mini-slump cone. In this case, the flow spread diameter of mixtures was 250-260 mm. The compressive strength of fine-grained concrete was determined on samples-prisms of 40x40x160 mm in size at 2, 7, 28 days, according to EN 196-1. The density of concrete at the age of 28 days was determined according to EN 12390-7. The open capillary porosity was measured by the water absorption method as the ratio of mass difference of water-saturated and dried samples to the concrete volume.

3. Results and discussion

The experiment plan and test results of fine-grained concrete with a cement-sand ratio 1:2 and different admixtures content are presented in table 1.
The binder ratio of self-compacting mortar mixtures can be achieved when the superplasticizer content is 1.2 %, and the silica fume content is 0 % by binder weight. If in mixtures with the same workability by 31 %. Replacing cement with silica fume due to the high specific surface of its particles leads to an increase in the water demand of mixtures without silica fume by 20 %. In the presence of 15 % silica fume, increasing the dosage of superplasticizer reduces the water-binder ratio of mixtures with the same workability by 31 %. Replacing cement with silica fume due to the high specific surface of its particles leads to an increase in the water-binder ratio of mixtures. If in mixtures with a minimum dosage of superplasticizer, the replacement of 15 % cement with silica fume led to an increase in W/B by 26 %, then with an increase in the dosage of superplasticizer, the effect of silica fume on the water demand of the mixtures gradually decreases. At a dosage of superplasticizer 1.2 %, the addition of 15 % silica fume only leads to a slight increase in W/B by 8 %. The minimum water-binder ratio of self-compacting mortar mixtures can be achieved when the superplasticizer content is 1.0-1.2 %, and the silica fume content is 0 % by binder weight.

Table 1. Experiment plan and test results.

| Plan points | Experiment plan | Average value of the response function |
|-------------|----------------|---------------------------------------|
|             | In coded variables | In natural variables | W/B | R₂, MPa | R₇, MPa | R₂₈, MPa | ρ, kg/m³ | Pₒ, % |
| X₁ | X₂ | SP, % | SF, % | Y₁ | Y₂ | Y₃ | Y₄ | Y₅ | Y₆ |
| 1 | -1 | -1 | 0.4 | 5 | 0.50 | 28.6 | 40.3 | 52.9 | 2138 | 12.19 |
| 2 | -1 | 0 | 0.4 | 10 | 0.54 | 24.9 | 37.8 | 51.6 | 2081 | 12.52 |
| 3 | -1 | +1 | 0.4 | 15 | 0.58 | 19.6 | 33.9 | 48.5 | 2028 | 13.38 |
| 4 | 0 | -1 | 0.8 | 5 | 0.41 | 37.9 | 54.3 | 74.0 | 2206 | 9.90 |
| 5 | 0 | 0 | 0.8 | 10 | 0.43 | 34.5 | 52.3 | 72.9 | 2178 | 9.25 |
| 6 | 0 | +1 | 0.8 | 15 | 0.45 | 30.4 | 47.1 | 72.2 | 2149 | 8.92 |
| 7 | +1 | -1 | 1.2 | 5 | 0.38 | 37.4 | 55.2 | 76.5 | 2228 | 9.15 |
| 8 | +1 | 0 | 1.2 | 10 | 0.39 | 36.1 | 56.8 | 79.6 | 2221 | 8.56 |
| 9 | +1 | +1 | 1.2 | 15 | 0.40 | 33.8 | 54.3 | 78.4 | 2219 | 7.72 |
| 10 | -1 | -2 | 0.4 | – | 0.46 | 31.8 | 44.9 | 55.2 | 2187 | 12.06 |
| 11 | 0 | -2 | 0.8 | – | 0.39 | 39.0 | 55.1 | 72.3 | 2230 | 10.24 |
| 12 | +1 | -2 | 1.2 | – | 0.37 | 33.8 | 49.6 | 68.0 | 2232 | 9.83 |

Based on the results of processing experimental data, regression models of responses are obtained, presented in table 2. The coefficient of determination of these regression models is close to 1, which indicates their high statistical significance.

Table 2. Regression models.

| Response | Regression model | R²a | SEEb |
|----------|-----------------|-----|------|
| W/B      | 0.432-0.075X₁+0.023X₂+0.033X₁²-0.015X₁X₂ | 0.997 | 0.003 |
| R₂       | 35.19+5.50X₁-3.28X₂-4.70X₁²-0.92X₁X₂+1.95X₂ | 0.973 | 0.73 |
| R₇       | 52.42+8.66X₁-2.51X₂-5.60X₁²-0.98X₁X₂+2.56X₂ | 0.946 | 1.39 |
| R₂₈      | 74.12+13.18X₁-0.69X₂-9.01X₁²-1.08X₂²+2.79X₁X₂ | 0.982 | 1.19 |
| ρ        | 2177+70.5X₁-29.0X₂-24.0X₁²-0.58X₁X₂+24.4X₂ | 0.999 | 1.73 |
| Pₒ       | 9.42-2.14X₁-0.19X₂+1.10X₁²+0.05X₁²-0.56X₂ | 0.974 | 0.22 |

a Coefficient of determination.
b Standard error of estimate.

Figure 1 shows the response surfaces of the obtained regression models depending on the content of superplasticizer and silica fume.

Analysis of the response surface of the water-binder ratio (figure 1 a) shows that increasing the dosage of the polycarboxylate superplasticizer Sika ViscoCrete 25 HE-C from 0.4 % to 1.2 % due to its plasticizing ability reduces the water demand of mixtures without silica fume by 20 %. In the presence of 15 % silica fume, increasing the dosage of superplasticizer reduces the water-binder ratio of mixtures with the same workability by 31 %. Replacing cement with silica fume due to the high specific surface of its particles leads to an increase in the water-binder ratio of mixtures. If in mixtures with a minimum dosage of superplasticizer, the replacement of 15 % cement with silica fume led to an increase in W/B by 26 %, then with an increase in the dosage of superplasticizer, the effect of silica fume on the water demand of the mixtures gradually decreases. At a dosage of superplasticizer 1.2 %, the addition of 15 % silica fume only leads to a slight increase in W/B by 8 %. The minimum water-binder ratio of self-compacting mortar mixtures can be achieved when the superplasticizer content is 1.0-1.2 %, and the silica fume content is 0 % by binder weight.
Figure 1. Response surfaces depending on the content of superplasticizer and silica fume:
(a) – water-binder ratio of mixtures with the same workability; (b) – compressive strength at 2 days;
(c) – compressive strength at 7 days; (d) – compressive strength at 28 days; (e) – density at 28 days; (f) – open capillary porosity at 28 days.
Analysis of regression models of the fine-grained concrete strength (figure 1 b-d) shows that increasing the dosage of superplasticizer from 0.4 % to 0.8 % in samples without silica fume can increase their strength at 2 days by 20 %, at 7 days – by 21 %, at 28 days – by 32 %. A further increase in the dosage of superplasticizer from 0.8 % to 1.2 % in mixtures without silica fume is ineffective due to a decrease in the strength of samples at 2 days by 8 %, at 7 days – by 3 %, at 28 days – by 3 %. In the presence of 15 % silica fume, increasing the dosage of superplasticizer from 0.4 % to 1.2 % leads to an increase in the concrete strength at 2 days by 79 %, at 7 days – by 67 %, and at 28 days – by 72 %.

It was found that in samples with a minimum dosage of superplasticizer, the replacement of 15 % cement with silica fume led to a decrease in the strength of fine-grained concrete by 40 %, 27 %, and 15 %, respectively. With an increase in the dosage of superplasticizer, the negative effect of silica fume on the strength of the samples gradually decreases. If at the dosage of superplasticizer of 0.8 %, the addition of 15 % silica fume leads to a decrease in the strength of fine-grained concrete at 2 days by 18 %, at 7 days – by 9 %, and at 28 days – to an increase in strength by 1 %. Then, at a dosage of superplasticizer of 1.2 %, already shows a decrease in the strength of concrete samples at 2 days by 3 %, and at 7 and 28 days – an increase in strength by 4 % and 14 %, respectively. The maximum compressive strength of fine-grained concrete at 2 days can be achieved with a superplasticizer content of 0.8-1.0 % and silica fume content of 0-5 % by binder weight, at 7 days – with a superplasticizer content of 0.9-1.1 % and silica fume content of 5-10 % by binder weight, at 28 days – with a superplasticizer content of 1.0-1.2 % and silica fume content of 10-15 % by binder weight.

Analysis of the concrete density at 28 days (figure 1 e) shows that increasing the dosage of polycarboxylate superplasticizer Sika ViscoCrete 25 HE-C from 0.4 % to 1.2 % in samples without silica fume allows increasing the density of fine-grained concrete by 2 %. In the presence of 15 % silica fume, increasing the dosage of superplasticizer leads to an increase in the density of fine-grained concrete by 9 %. Replacing cement with silica fume due to its increased water demand leads to a decrease in the concrete density. If in mixtures with a minimum dosage of superplasticizer, the replacement of 15 % cement with silica fume led to a decrease in density by 7 %, then with an increase in the dosage of superplasticizer, the effect of silica fume on the decrease in density gradually decreases. At a dosage of superplasticizer 1.2 %, the addition of 15 % silica fume only leads to a slight decrease in density by 0.5 %. The maximum density of fine-grained concrete at 28 days can be achieved with a superplasticizer content of 0.8-1.2 % and a silica fume content of 0 % by binder weight.

Analysis of the open capillary porosity of concrete (figure 1 f) shows that increasing the dosage of polycarboxylate superplasticizer Sika ViscoCrete 25 HE-C from 0.4 % to 0.8 % in samples without silica fume reduces the open capillary pores volume by 17 %. However, a further increase in the dosage of superplasticizer from 0.8 % to 1.2 % in mixtures without silica fume does not lead to a decrease in the concrete porosity. In the presence of 15 % silica fume, increasing the dosage of superplasticizer from 0.4 % to 1.2 % leads to a decrease in capillary porosity of the samples by 41 %. It was found that in samples with a minimum dosage of superplasticizer, the replacement of 15 % cement with silica fume led to an increase in capillary porosity of fine-grained concrete by 8 %. With increasing the dosage of superplasticizer, a positive effect of silica fume on a decrease in the concrete porosity due to its microfilling effect is observed. If at a dosage of superplasticizer 0.8 %, the addition of 15 % silica fume leads to a decrease in the capillary porosity of concrete by 7 %, and then at a dosage of superplasticizer 1.2 % a decrease in the open capillary pores volume is already 24 %. The minimum capillary porosity of fine-grained concrete at 28 days can be achieved with a superplasticizer content of 1.2 % and silica fume content of 15 % by binder weight.

Thus, the experimental studies showed the effectiveness of combined use of superplasticizer and silica fume to improve the physical and mechanical characteristics of self-compacting concrete, and allowed to determine the optimal dosages of organomineral modifier components in terms of increasing the early and design concrete strength and reducing its porosity: 1 % of polycarboxylate superplasticizer Sika ViscoCrete 25 HE-C and 10 % of silica fume MK-85 by binder weight.
To identify the pattern of changes in the phase composition during hydration and structure formation of cement systems with superplasticizer and silica fume, an X-ray phase analysis of cement stone samples was performed. Figure 2 shows X-ray diffraction patterns of the control composition of cement stone without admixtures (a) and with superplasticizer and silica fume (b) at 28 days.

It was found that the use of silica fume and superplasticizer leads to a slight decrease in the diffraction reflection intensity of unreacted clinker minerals: alite \( d = [3.03; 2.77; 2.60; 2.32; 2.18 \text{ Å}] \), belite \( d = [2.88; 2.29 \text{ Å}] \) and brownmillerite \( d = [7.28; 3.66; 2.67; 2.05 \text{ Å}] \). It allows us to conclude that these admixtures accelerate cement hydration processes at 28 days.

Despite the increase in the degree of clinker minerals hydration in the sample with admixtures, the amount of formed portlandite \( d = [4.91; 3.11; 2.63; 1.93 \text{ Å}] \) is almost halved compared to the control sample. The decrease in the amount of portlandite is associated with the pozzolanic reaction of amorphous silicon dioxide in the late stages of cement hardening with the formation of low-basic hydrated calcium silicates. A decrease in ettringite is also observed, as evidenced by diffraction reflections with interplanar spacings \( d = [9.73; 5.61; 4.70; 3.87 \text{ Å}] \).

4. Conclusions
1. Regression models of the superplasticizer and silica fume influence on the properties of self-compacting mortars were obtained, with the help of which the role of each component of the organomineral modifier on the structure formation of self-compacting concrete was studied.

2. It was found that the replacement of cement with silica fume due to the high specific surface of its particles leads to an increase in the water-binder ratio of mixtures with the same workability up to 30 %. The use of polycarboxylate superplasticizer due to its plasticizing ability allows reducing the water-binder ratio of mixtures up to 40 %.

3. The maximum compressive strength of fine-grained concrete at 2 days can be achieved with a superplasticizer content of 0.8-1.0 % and silica fume content of 0-5 % by binder weight. A further increase in the dosage of superplasticizer to 1.2% and silica fume to 10-15% is ineffective due to a decrease in the strength of concrete.

4. The positive effect of silica fume on the concrete compressive strength at 28 days in compositions with a high content of superplasticizer was noted. In this case, there is an increase in the
strength of concrete to 14%. The maximum strength of fine-grained concrete at 28 days can be achieved with a superplasticizer content of 1.0-1.2 % and silica fume content of 10-15 % by binder weight.

5. The positive effect of silica fume on reducing the concrete porosity due to its microfilling effect is shown. If at a dosage of superplasticizer 0.8 %, the addition of 15 % silica fume leads to a decrease in the capillary porosity of concrete by 7 %, and then at a dosage of superplasticizer 1.2 % a decrease in the open capillary pores volume is already 24 %. The minimum capillary porosity of fine-grained concrete at 28 days can be achieved with a superplasticizer content of 1.2 % and silica fume content of 15 % by binder weight.

6. According to results of the study, for preparation of self-compacting concrete mixtures in terms of increasing the early and design concrete strength and reducing its porosity, the optimal organomineral modifier composition is the dosage of superplasticizer Sika ViscoCrete 25 HE-C of 1 % by binder weight and the dosage of silica fume MK-85 of 10 % by binder weight.

7. According to the results of X-ray phase analysis, it was found that the use of silica fume and superplasticizer leads to an increase in the degree of clinker minerals hydration at 28 days. At the same time, there was a significant decrease in the amount of portlandite in samples with admixtures, associated with the pozzolanic reaction of amorphous silicon dioxide with the formation of low-basic hydrated calcium silicates.

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