ISSN 1819-432X print / ISSN 1993-3495 online
СУЧАСНЕ ПРОМИСЛОВЕ ТА ЦИВІЛЬНЕ БУДІВНИЦТВО
СОВРЕМЕННОЕ ПРОМЫШЛЕННОЕ И ГРАЖДАНСКОЕ СТРОИТЕЛЬСТВО
MODERN INDUSTRIAL AND CIVIL CONSTRUCTION
2015, ТОМ 11, НОМЕР 4, 189–197
УДК 666.031

РЕОЛОГІЧНІ ВЛАСТИВОСТІ ЦЕМЕНТНИХ ПАСТ У СКЛАДІ САМОУЩІЛЬНЮВАЛЬНОГО БЕТОНУ З ПОЛІФУНКЦІОНАЛЬНИМ МОДИФІКАТОРОМ

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Отримана 16 листопада 2015; прийнята 25 грудня 2015.

Анотація. Реологічні властивості цементних паст, що використовуються у складах самоущільнювальних бетонів, досліджено з метою встановлення ефективності впливу поліфункціонального модифікатора на властивості свіжовідформованого та затверділого бетону. Встановлено, що поліфункціональний модифікатор у вигляді концентрованої суспензії мікрокремнезему в розчині гідроксиду натрію та суперпластифікатора на основі поліметиленнафталінсульфонату впливає на реологічні властивості цементних паст, знижуючи пластичну в'язкість і слабко зменшуючи значення межі текучості. Встановлено закономірності впливу реологічних властивостей цементної пасти з органо-мінеральним модифікатором на властивості самоущільнювальної бетонної суміші (текучість, час течії T_{500}, проникна здатність, опір сегрегації). Лужний компонент у складі поліфункціонального модифікатора дозволяє здійснити часткову заміну (35–45 %) портландцементу меленим доменним гранульованим шлаком.

Ключові слова: самоущільнювальний бетон, цементна паста, реологічні властивості, поліфункціональний модифікатор, пластична в'язкість, граничне напруження зсуву, текучість, опір сегрегації.

РЕОЛОГИЧЕСКИЕ СВОЙСТВА ЦЕМЕНТНЫХ ПАСТ В СОСТАВЕ САМОУПЛОТНЯЮЩЕГОСЯ БЕТОНА С ПОЛИФУНКЦИОНАЛЬНЫМ МОДИФИКАТОРОМ

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Получена 16 ноября 2015; принята 25 декабря 2015.

Аннотация. Реологические свойства цементных паст, используемых в составах самоуплотняющихся бетонов (СУБ), исследованы с целью установления эффективности влияния полифункционального модификатора на свойства свежеотформованного и затвердевшего бетона. Установлено, что полифункциональный модификатор в виде концентрированной суспензии микрокремнезема в растворе гидроксида натрия и суперпластификатора на основе полиметиленнафталинсульфоната оказывает влияние на реологические свойства цементных паст снижая пластическую вязкость и слабо уменьшая значение предела текучести. Установлены закономерности влияния реологических свойств цементной пасты с органо-минеральным модификатором на свойства самоуплотняющейся бетонной смеси (текучесть, время течения T_{500}, проникающая способность, сопротивление сегрегации). Щелочной компонент в составе полифункционального модификатора позволяет осуществить частичную замену (35–45 %) портландцемента молотым доменным гранулированным шлаком.

Ключевые слова: самоуплотняющийся бетон, цементная паста, реологические свойства, полифункциональный модификатор, пластическая вязкость, предельное напряжение сдвигу, текучесть, сопротивление сегрегации.

THE RHEOLOGICAL PROPERTIES OF CEMENT PASTES FORMULATED FOR SELF-COMPACTING CONCRETES WITH MULTIFUNCTIONAL MODIFIER

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Received 16 November 2015; accepted 25 december 2015.

Abstract. The rheological properties of cement pastes formulated for self-compacting concretes (SCC) were used to investigate the efficiency of multifunctional modifier on the properties of fresh and hardened concrete. It was found that the multifunctional modifier in the form of the concentrated suspension of silica fume in the solution of polynaphthalene sulfonate condensate superplasticizer and sodium hydroxide affects the rheological properties of cement paste, decreasing plastic viscosity and slightly decreasing the value of yield stress. The regularities of the influence of the rheological properties of cement pastes with organic-mineral modifier on the properties of fresh self-compacting concrete (flowability; T_{500} slump flow time; passing ability; resistance to segregation) were determined. An alkaline component of the multifunctional modifier allows to perform a partial replacement (35–45 %) of the Portland cement with ground granulated blast furnace slag.

Keywords: self-compacting concrete, cement paste, rheological properties, multifunctional modifier, plastic viscosity, yield stress, flowability, resistance to segregation.

Introduction

Self-compacting concrete (SCC) is an innovative concrete that does not require vibration for placing and compaction. It is able to flow under its own weight, completely filling formwork and achieving full compaction, even in the presence of congested reinforcement. The hardened concrete is dense, homogeneous and has the same engineering properties and durability as traditional vibrated concrete [1, 2]. Self-compacting concrete is defined as a special type of concrete which must fulfil the following three basic properties [1–5]:

- filling ability: concrete must be able to flow freely both in horizontal and vertical direction – even upwards if needed, and fill the formwork of almost any shape completely under its own weight only;
- passing ability: concrete is not allowed to cause any blocking when passing through narrow gaps caused by the geometry of the formwork or by a dense reinforcement grid;
- stability: during mixing, placement and after casting, concrete is not allowed to segregate, causing an inhomogeneous mixture.

These three basic properties, combined with the absence of the need for compaction make the application of SCC very advantageous in cases of complex geometries of the formwork, cases with dense reinforcement grids and difficultly attainable places [5]. Fluidity and resistance to segregation of SCC ensure high degree of homogeneity with minimal content of voids and uniform strength, high degree of surface quality and high durability [6].

It's well known [7] that pumping, spreading, moulding and compaction of concrete mixtures all depend on rheology and thanks to an increasingly scientific approach it is becoming possible to predict fresh properties, design and select materials and model processes to achieve the required performance. Nowadays the rheological behaviour of pastes, mortars and concretes continues to be a subject of analysis in light of the large number of factors involved in cement blending, mixing and hydration (such as type of cement, type and proportions of mineral additions and presence or otherwise of admixtures). For this reason, it is necessary to identify concrete incompatibilities before concrete placement in order to avoid the problems in the placing and curing processes [8].

So, cement paste rheology measurements instead of traditional workability tests can have a great potential to detect those incompatibilities in concrete before the concrete is placed [7]. For example, avoiding segregation of SCC is a matter of cement paste rheology and granular skeleton. The cement paste has to be sufficiently fluid to ensure the fluidity of the concrete itself and sufficiently viscous to support the coarse aggregates [9].

The major difference in composition of traditional and self-compacting concrete lies in higher proportion of fine parts by 30–40 % by volume. As a rule, SCC often contains a large quantity of powder mineral additives such as fly ash, bottom ash, granulated blast furnace slag or limestone filler which are required to maintain sufficiently low yield stress to provide flowability at a plastic viscosity which is high enough to avoid segregation [10, 11].On the other hand, the sedimentation rate of coarse aggregate in the cement matrix can be reduced effectively by increasing the content of fines with high specific density – density modifiers, and with regards to fines, the best density modifier is granulated blast furnace slag. Thereby, in most cases, addition of fly ash and silica fume does not affect the matrix density [12].

However, concretes with high percentages of slag often have lower early strength and longer setting time than Portland cement concrete without slag. In this case according to [13] the incorporation of 2 % colloidal nanosilica (CNS) by mass of cementitious materials reduces initial and final setting time, and increases early compressive strengths of high-volume slag concrete by 22 %, in comparison to the reference concrete with 50 % slag. The similar effect has been determined in fly ash – cement mortars: the early-age compressive strength of fly ash – cement mortars can be greatly improved by the addition of CNS [14].The main mechanism of accelerating effect in cement is related to the high surface area of CNS, because it works as nucleation site for the precipitation of CSH-gel. On the other hand, nano-silica is applied in HPC and SCC concretes mainly as an anti-bleeding agent. It is also added to increase the cohesiveness of concrete and to reduce the segregation tendency [15].

In our previous investigations [16, 17] the resource-saving method provided a stable aqueous silica fume suspension containing 20 to 45 % by weight of silica fume which is a by-product of ferrosilicon production and a stabilizing agent in a form of high range water reducing admixture (polynaphthalene sulfonate condensate) as well as sodium hydroxide (sulphate) was elaborated. This composition has been found highly suitable as a multifunctional modifier for cementitious compositions in particular for self-compacting concrete to enhance its flowability as well as durability and strength characteristics. It should be noted also that the presence of sodium hydroxide in the composition of above mentioned complex admixture makes it possible to use granulated blast furnace slag as a partial replacement of Portland cement in the formulation of concrete mixtures. The results obtained by [18] indicate a high effectiveness of the composition of silica fume with alkali admixture as an activator for the binding systems based on the combination of Portland cement, silica fume and granulated blast furnace slag.

The aim of this investigation is to determine the effect of multifunctional modifier on the rheological properties of cement pastes formulated for SCC and the properties of fresh and hardened self-compacting concrete.

Materials and methods

Ordinary Portland cement CEM I 42.5 N (OPC), silica fume (SF) and granulated blast furnace slag (GBFS) were used as cementitious materials. Silica fume was represented as small and big aggregates which were formed during drying silica fume slurry in sludge collectors (when silica fume slurry is disposed in landfills and its water content is drastically reduced). It is stipulated by gelling and the condensation polymerization accompanied with the formation of siloxane linkages. Thus, aged agglomerated silica fume aqueous suspensions need to be redispersed before use in concrete. This process occurred in the solution of sodium hydroxide (sodium sulphate) and polynaphthalene sulfonate condensate (PNS).

Dispersing aggregates of aged agglomerated silica fume was carried out in the bead mill, used to produce ultrafine products in a liquid medium by grinding the slurry material with solid balls – glassy beads. Bead mill is a cylindrical vessel with a mixing rotor, providing different modes of mixing and circulation of beads. The mill is filled with the glassy beads for 70–80 % of the volume. The beads are moved by rotation of the mill rotor (duration of grinding – 10 minutes).

Quartz sand and crushed granite stone with a maximum nominal size of 20 mm and a specific gravity (dry) of 2.68 were used as fine and coarse aggregates respectively. The chemical composition and physical properties of cementitious materials are given in Table 1.

The proportions of cement pastes with the multifunctional modifier are summarized in Table 2. The water demand (w/cm ratio) was varied to prepare a standard consistency of cement pastes.

The rheological behaviour of a fluid such as cement paste, mortar or concrete is most often characterized by at least two parameters, τ_0 and μ, as defined by Bingham equation [19]:

$$\tau = \tau_0 + \mu\dot{\gamma}\,, \tag{1}$$

where τ is the shear stress applied to material (Pa), τ_0 is the yield stress (Pa), μ is the plastic viscosity (Pa · s), and $\dot{\gamma}$ is the shear strain rate (s^{-1}).

Shear stress values, as well as plastic viscosity of cement pastes at different shear rates were obtained using Rheometer RHEOTEST® RN4.1 (RHEOTEST Medingen GmbH) with cone-and-plate measuring system according to DIN 53018 (Fig. 1).The paste was mixed manually for 5 minutes in a porcelain crucible and poured into the viscometer annulus.

The proportions of self-compacting concretes with and without multifunctional modifier are summarized in Table 3. The stability of SCC was tested according to ASTM C1610/C1610M-10 «Standard Test Method for Static Segregation of Self-Consolidating Concrete Using Column Technique».

This test method covers the determination of static segregation of self-consolidating concrete by measuring the coarse aggregate content in the top and bottom portions of a cylindrical column (mold). A sample of freshly-mixed self-consolidating concrete is placed in a cylindrical mold without tamping or vibration. The mold is separated into three sections representing different levels of the cylindrical specimen (or column). Portions of concrete from the top and bottom section are washed on a 5 mm sieve, leaving the coarse aggregate on the sieve. The masses of coarse aggregate in the top and the bottom sections are determined and the percent static segregation is calculate dusing the following equation:

$$S = 2\left[\frac{(CA_B - CA_T)}{(CA_B + CA_T)}\right]\cdot 100\,, \tag{2}$$

where S is static segregation, percent, C_{AT} is the mass of coarse aggregate in the top section of the column, C_{AB} is the mass of coarse aggregate in the bottom section of the column.

Table 1. Chemical composition and properties of the materials used

Composition (%) Properties	OPC	GBFS	SF	
SiO_2	21.40	34.80	81.80	
Al_2O_3	5.80	13.40	1.60	
Fe_2O_3	3.40	0.70	3.00	
CaO	61.50	39.80	1.10	
MgO	1.70	6.50	0.20	
K_2O	0.70	0.10	0.60	
SO_3	2.50	0.35	3.60	
Loss on ignition	1.20	3.60	7.20	
Specific gravity	3.11	2.92	2.20	0.14 – 20.00 mm aggregates
Fineness ($m^2 \cdot kg^{-1}$)	365.00	414.00	–	

Table 2. The proportions of cement pastes with multifunctional modifier

Mixture	OPC, g	GBFS, g	SF, g	PNS, g	NaOH, g	w/cm
CP 1	100	–	–	–	–	0.260
CP 2	100	–	–	1.2	–	0.210
CP 3	–	100	–	–	1.5	0.270
CP 4	65	35	–	–	1.5	0.260
CP 5	65	35	–	1.2	1.5	0.230
CP 6	65	35	7.5	1.2	1.5	0.265

Figure 1. Rheometer RHEOTEST® RN 4.1.

Experimental results and discussion

Figure 2 reports the plastic viscosity of cement pastes versus shear rate in the 30–270 s^{-1} rang. The maximum value of the initial plastic viscosity at a minimum shear rate of 30 s^{-1} has the reference cement paste (CP 1) with w/cm = 0.26. When the PNS superplasticizer is added the water demand of cement paste (CP 2) is decreased up to w/cm = 0.21. In this case the initial value of the plastic viscosity is reduced almost two times and the equilibrium plastic viscosity at the shear rate 240–270 s^{-1} reaches the smallest value among all investigated compositions of cement pastes. This is because floccules of cement are better dispersed by the electrostatic effect of superplasticizer, so entrapped water can contribute to the fluidity of cement paste.

The greatest water demand has a granulated blast furnace slag when mixing with tap water – w/cm = 0.285. At the same time, the addition of sodium hydroxide has a weak plasticizing effect, reducing water demand of slag paste (CP 3) up to w/cm = 0.27.

Thus, the ratio «initial plastic viscosity/equilibrium plastic viscosity» within the shear rate range 30–270 s^{-1} is 5.7 while for cement pastes compositions CP 1 and CP 2 is 12.9 and 10.7, respectively. Partial replacement of Portland cement with granulated blast furnace slag in an amount of 35 % slightly increases the water demand and plastic viscosity of cement paste (CP 4). At the same time a positive effect of complex additive in the form of SP + sodium hydroxide to reduce these figures was determined (CP 5). On the other hand, a relatively small content of silica fume increases significantly enough both a water demand and the plastic viscosity of cement paste (CP 6). This effect however has a positive impact on the stability of SCC. Concrete mixture with multifunctional modifier has the higher coefficient of resistance to segregation in comparison with reference formulation of SCC (Tab. 4).

It should be noted also that no significant effect of multifunctional modifier on the values of yield stress of cement paste was determined. This fact must be taken into account because all SCC must have relatively low yield stress values in order to self-consolidate. So, in accordance with the European Guidelines for Self-Compacting Concrete [1] the investigated SCC with the multifunctional modifier (SCC-2) refers to the next classes: SF1 (Slump-flow, mm), VS1/ VF1 (T_{500}, s), PA2 (Passing ability), SR2 (Segregation resistance, %). Therefore, with respect to the rheological parameters, once the slump flow level has been established, it is primarily the plastic viscosity that is manipulated in order to control performance.

For hardened concrete it has been established that the presence of sodium hydroxide in the formulation of multifunctional modifier activated concrete hardening both at early and design age (Tab. 4).

Table 3. The proportions of self-compacting concretes

Mixture	Content of ingredients, kg·m^{-3}							
	OPC	Fine aggregate	Coarse aggregate	SF *	GBFS	PNS	Sodium hydroxide	w/cm
SCC-1	442	885	796	–	–	6.64	–	0.48
SCC-2	287	885	746	33.5	155	6.64	6.65	0.48

* Dry content.

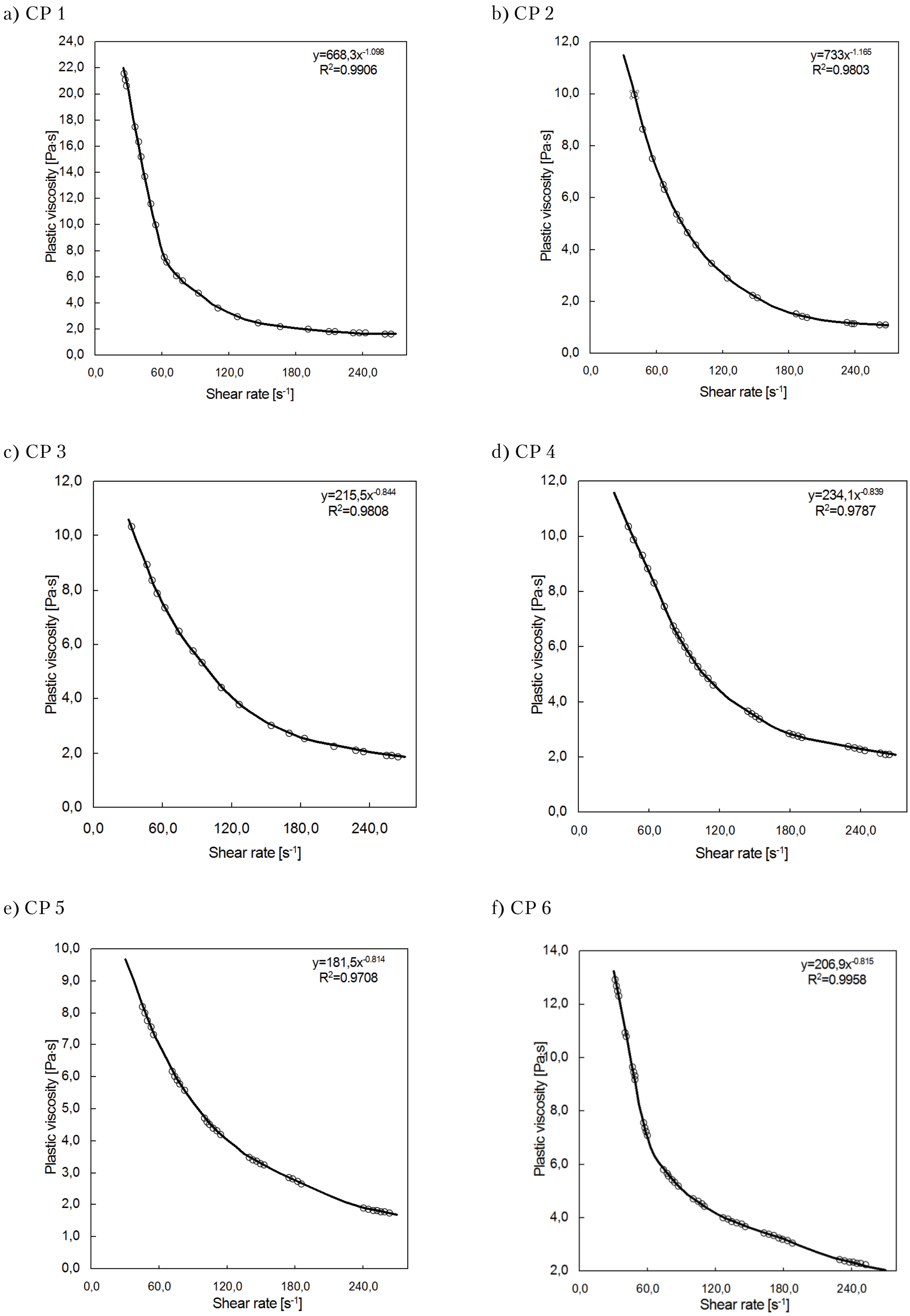

Figure 2. Plastic viscosity of cement pastes versus shear rate.

Table 4. The properties of cement pastes and self-compacting concretes

Mixture	Properties							
	Yield value, Pa	Slump flow, mm	T_{500} time, s	$PA = \frac{H2}{H1}$	SR, %	Compressive strength, MPa		
						3 days	7 days	28 days
CP 1	58.7	–	–	–	–	18.5	27.4	52.4
CP 2	56.5	–	–	–	–	26.8	39.8	67.3
CP 3	56.9	–	–	–	–	2.3	6.7	14.4
CP 4	57.0	–	–	–	–	16.4	23.6	43.3
CP 5	57.1	–	–	–	–	19.5	32.1	55.7
CP 6	57.4	–	–	–	–	22.3	43.5	61.2
SCC-1	–	540	2.0	0.86	13.7	12.2	25.7	36.4
SCC-2	–	565	2.0	0.82	9.5	21.4	32.4	45.8

Conclusion

It was found that the multifunctional modifier in the form of the concentrated suspension of silica fume in the solution of polynaphthalene sulfonate condensate superplasticizer and sodium hydroxide affects the rheological properties of cement paste, decreasing plastic viscosity and slightly decreasing the value of yield stress. Partial replacement of Portland cement with granulated blast furnace slag in an amount of 35 % slightly increases the water demand and plastic viscosity of cement paste. At the same time a positive effect of complex additive in the form of SP + sodium hydroxide to reduce these figures was determined. On the other hand, a relatively small content of silica fume significantly enough increases both a water demand and the plastic viscosity of cement paste. This effect however has a positive impact on the stability of SCC. An alkaline component of the multifunctional modifier allows to perform a partial replacement of the Portland cement with granulated blast furnace slag.

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