

BEHAVIOR OF SUPERPLASTICIZED CEMENTITIOUS SYSTEMS FOR SELF-COMPACTING CONCRETE

*Department of Building Production,
Lviv Polytechnic National University
iryna.i.kirakevych@lpnu.ua*

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The article presents the peculiarities of obtaining superplasticized cementitious systems "Portland cement – fly ash - superplasticizer" to find a rational provision of the given construction and technical properties of concrete. It was studied the physico-chemical peculiarities of the hydration processes of superplasticized cementitious systems. There were solved problems of directional formation of the microstructure of cement stone. Research results show that the use of superplasticized cementitious systems allows influencing the technological properties and kinetics of structure formation and creating a dense and strong microstructure of the concrete cementitious matrix. The use of superplasticized cementitious systems solves the problems of obtaining rapid-hardening self-compacting concrete, which creates the possibility of using vibration-free technology of monolithic concreting of structures.

Keywords: Portland cement, superplasticizer, fly ash, superplasticized cementitious system, self compacting concrete, high strength.

Introduction

A promising direction in monolithic construction for the creation of self-compacting concrete with a rapid hardening is the use of superplasticized cementitious systems with high early strength (Shi, Bo, & Provis, 2019). Targeted regulation of the rheological parameters of cementitious systems and the processes of their early structure formation is a prerequisite for the creation of new generation structural materials with specified construction and technical properties (Szwabowski, & Golaszewski, 2004).

Monolithic concreting requires the use of concrete mixtures of increased flowability with leveling in heavily reinforced structures, spontaneous removal of entrapped air, preservation of uniformity and elimination of delamination of components during placing and transportation. This leads to the use of complex chemical and mineral additives. Self-compacting concrete is characterized by a multi-component composition, which requires to use chemical additives, in particular superplasticizers of the polycarboxylate type (PC). In order to ensure improved performance of structural materials, there is a need to study the effect of PC on the properties and structure formation of Portland cement systems (Urban, 2018).

The purpose of the work is to study the processes of structure formation of superplasticized cementitious systems "Portland cement - fly ash - polycarboxylate superplasticizer" for self-compacting concrete in the early period of hardening, establishing the peculiarities of their hydration processes.

Materials and Methods

Portland cement CEM I 42.5 PJSC "Ivano-Frankivskcement", fly ash of Burshtyn TPS (FA) and superplasticizer of the polycarboxylate type (PC) were used for the preparation of superplasticized cementitious systems during the experiments. With the use of X-ray phase analysis and scanning electron microscopy, the peculiarities of the hydration processes of superplasticized cementitious systems were investigated.

Results and discussion

The basis of self-compacting concrete is a free-flowing paste that ensures high flowability of the mixture without phase segregation during transportation and forming (Dvorkin, Bezusyak, Lushnikova, & Ribakov, 2012). The flowability of the paste improves with an increase in the thickness of the water layer on the surface of the particles. Thus, in order to ensure high flowability of the paste based on CEM I 42.5 and fly ash (the flow rate behind the Suttard cylinder, SC=320 mm), it is necessary to increase the amount of mixing water to W/C=0.60 (Fig. 1). The authors established (Pang, Liu, Wang, & An, 2022) that the fluidity of cement paste can be estimated by the coefficient of relative fluidity of cohesive systems (I_r) according to formula (1):

$$I_r = \frac{(W/C)/(WD) - 0.876}{0.774} \quad (1)$$

where W/C – water-cement ratio; WD – water demand.

The equation for evaluating the fluidity of cohesive systems shows that a Portland cement with a high water content (W/C=0.60) is not cohesive ($I_r = 1.5$) and is characterized by a bleeding of 3-5%, which causes its - segregation. At the same time, the superplasticized Portland cement system containing 2 wt.% of PC (W/C=0.30) is cohesive ($I_r = 0.2$) and flowable.

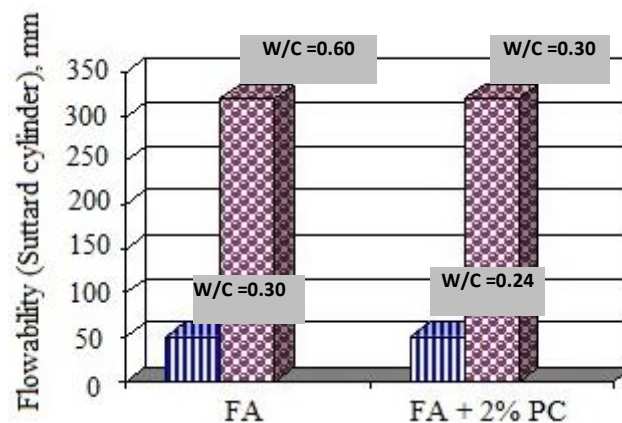


Fig. 1. Effect of fly ash and polycarboxylate on the flowability of Portland cement systems

As a result of the research, it was found that when the Portland cement system based on CEM I 42.5 and fly ash (W/C=0.30) is included, 0.25; 0.50; 1.0 and 2.0 wt.% polycarboxylate PC, the flow rate behind the Suttard cylinder increases from 50 to 250; 285; 290 and 320 mm, respectively. The main functions of fly ash in cement systems are to fill the intergranular space and improve rheological properties due to its spherical shape (Łaźniewska-Piekarczyk, 2014). With optimal dosing, FA reduces the water demand of the cement system and increases its flowability (Aicha, 2020). This can be explained by the fact that the spherical particles of FA perform the function of "rolling bearings", reducing the friction between the particles (Bitouri, Azéma, Saoût, Lauten & Weerd, 2022).

The initial W/C per unit volume determines the concentration of cement particles and the distance between them until the moment of structure formation - the setting. The results of determining the setting time of cement paste (1:0) based on CEM I 42.5 and fly ash established that the introduction of 1.0 wt.% PC with a simultaneous water-reducing effect ($\Delta W/C = 37\%$) slows down the initial setting time for 1 hour 40 min, and the finish - for 3 hours 20 min with a relatively uniform paste without additives (Sanytsky, Kropyvnytska, Kirakevych, & Rusyn, 2013). The greater the distance between the cement grains, the later the initial and finish setting time occurs in the system without additives (Jamrozy, 2000). Increasing the water demand of the cement system without additives from 0.30 to 0.60 causes the start of hardening to be delayed to 6 h 40 min, and the end of hardening to 9 h 10 min (Fig. 2). The onset of

hardening of the superplasticized Portland cement system in conditions of reduced water content ($W/C=0.24$) is delayed to 4 h 10 min, and the end to 8 h 10 min. At the same time, the first stage of structure formation of the paste without additives ($W/C=0.30$) takes place up to 3 hours. The introduction of 2.0 wt.% PC does not extend the period between the initial setting time (Fic, 2019).

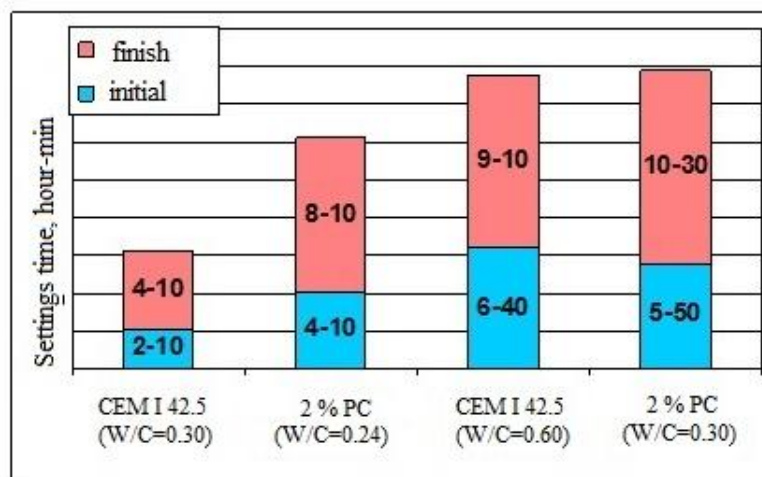


Fig. 2. Setting time of cement systems with polycarboxylate superplasticizer

Strength of paste based on CEM I 42.5 ($WD=0.30$, $SC = 50$ mm) under normal conditions hardening after 2; 7 and 28 days is 29.9; 45.5 and 50.1 MPa. At the same time, for the superplasticized Portland cement system ($RC = 250-320$ mm), the strength reaches to 31.9; 54.8 and 60.8 MPa, respectively. The obtaining the necessary hardening speed and dense structure of self-compacting concrete is achieved by using superplasticized binders with the following effects: high packing density of cementitious system grains due to the use of highly dispersed compositions (physical optimization); pozzolanic reaction when using fly ash (chemical optimization); by increasing the adhesion between the cement matrix and the aggregate (optimization of the concrete mesostructure) (Kirakevych, Sanytsky, & Margal, 2020).

On the other hand, hardening of the superplasticized Portland cement system is accompanied by significant loss of mass of the samples in the initial period. The amount of water remaining is insufficient for hydration (Plugin, Kaliuzhna, Borziak, Plugin, & Savchenko, 2021). Therefore, over time, the reverse process of adsorption of water and carbon dioxide from the air is observed (Gołaszewski, 2017). A decrease in the internal relative humidity leads to the emergence of capillary forces in the pores, which lead to a decrease in the volume of the artificial stone ("self-dehydration" or "self-drying" process) (Collepari, & Valente, 2006). Samples based on the superplasticized Portland cement system are characterized by intensive changes in mass under different hardening conditions (Lukowski, 2016). As can be seen from Fig. 3, the change in mass of paste samples under normal hardening conditions occurs after 4 days. Thus, the mass loss of modified paste under normal conditions after 4 days of hydration is 3 times greater compared to the loss of paste based on CEM I 42.5 and fly ash and is 7.5%. After 28 days of hydration, the increase in water content of the stone is 1.7%.

It was established that the strength of paste based on superplasticized cementitious systems is higher by 15-30% compared to the paste based on system «CEM I 42.5 – FA» and is 29.9 MPa after 2 days. The strength of the paste after 28 days of hardening on the basis of CEM I 42.5 and fly ash is 50.1 MPa. When 0.25; 0.50; 1.00; 2.00 wt.% PC was introduced the strength increases to 58.5; 52.0; 59.8; 60.8 MPa, respectively.

Using the methods of physical and chemical analysis, the peculiarities of the hydration of cement paste based on cement systems "CEM I 42.5 - FA" and "CEM I 42.5 - FA - PC" were studied under normal conditions ($t=20\pm 3$ °C, $\phi\geq 95\%$). The analysis of diffractograms shows (Fig. 4) that the main products of hydration are ettringite ($d/n=0.973$; 0.561 nm) and portlandite ($d/n=0.493$; 0.263 nm). In

diffractogram of the paste based on superplasticized cementitious system the intensity of the line of alite ($d/n=0.218$ nm) decreases compare to system «CEM I 42.5 - FA».

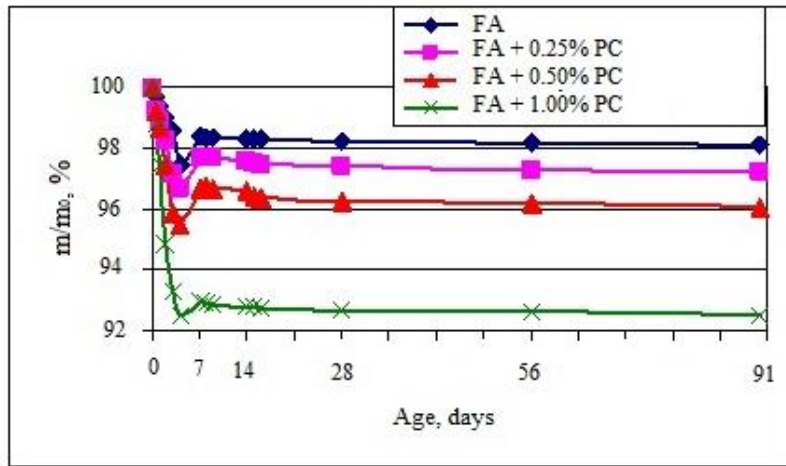


Fig. 3. Change in mass of cement paste based on superplasticized cementitious systems «CEM I 42.5 – FA – PC»

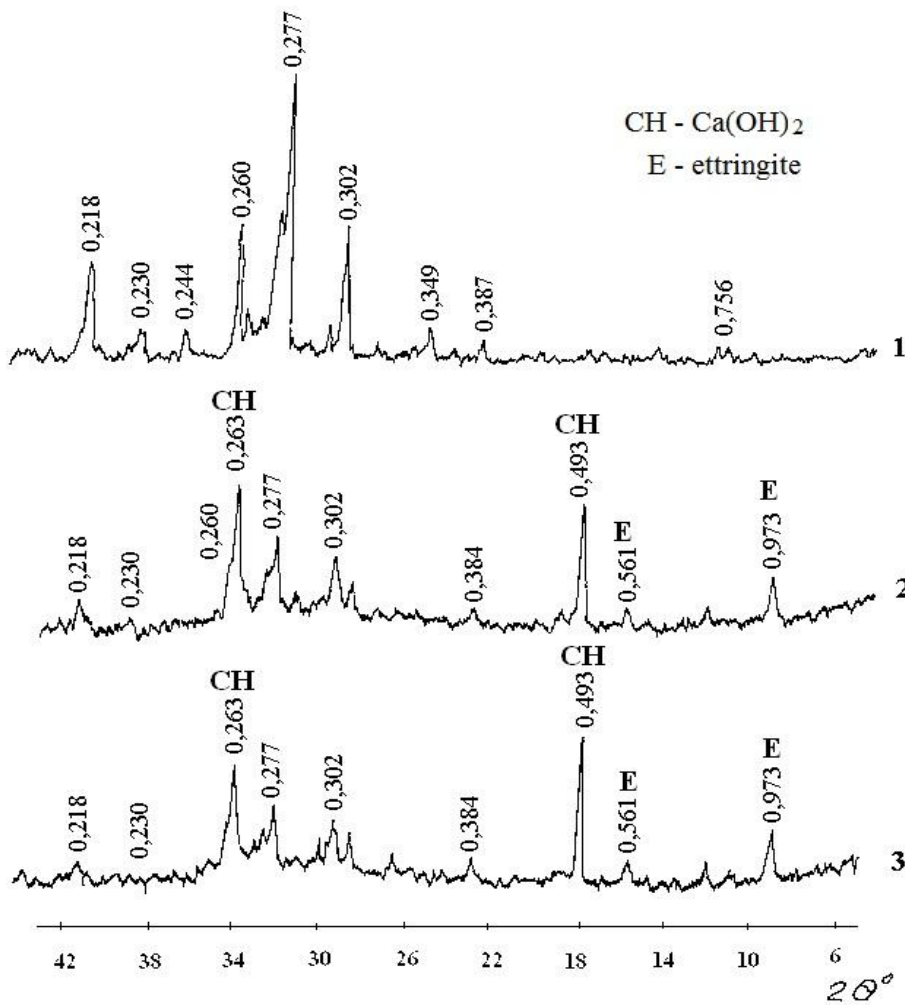


Fig. 4. Diffractograms of the paste:
 1 – unhydrated CEM I 42.5; 2-3 – hydrated 28 days, respectively, on the basis of CEM I 42.5 - FA and superplasticized cementitious system

The study of cement paste was carried out using electron microscopy after 28 days of hardening. It has been established that the stone based on CEM I 42.5 and FA is characterized by the presence of pores in which the growth of hydration products, in particular, tangled crystals of calcium hydrosilicates occurs (Plank, Sakai, Miao, Yu, & Hong, 2015). A paste based on a superplasticized Portland cement system is characterized by a rather dense microstructure with a small number of pores that have already become overgrown with hydration products or are in the stage of overgrowth. The size of the crystals that make up the blocks reaches 10 μm (Fig. 5, a). From Fig. 5, b, it can be seen that the pore is covered by needle crystals of ettringite in the paste. This allows us to assert the high efficiency of PC in superplasticized cement systems.

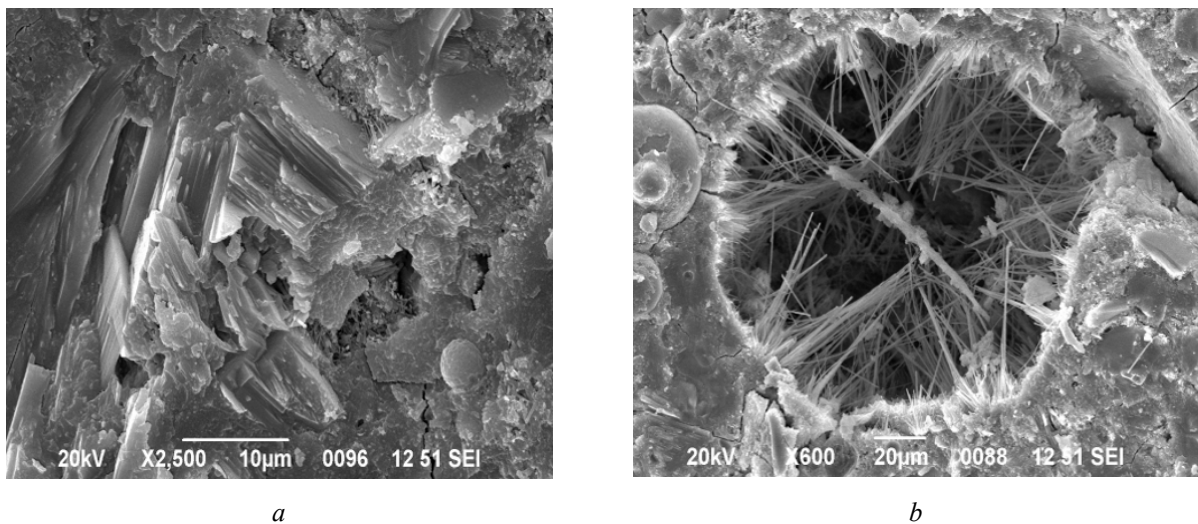


Fig. 5. Microstructure of paste based on superplasticized cementitious systems after 28 days of hardening

Analysis of microstructure formation shows that the use of superplasticized cementitious systems compacts the cement matrix due to the formation of fine-crystalline ettringite crystals and pore clogging with hexagonal portlandite crystals. This leads to a redistribution of porosity and an increase of paste strength (Gamze Erzenin, Kaya, Perçin Özkorucuklu, Özdemir, & Gizem, 2018).

Conclusions

Therefore, providing high rheological indicators of Portland cement systems requires the use of polycarboxylate superplasticizers of a new generation. It was established that the use of fly ash and polycarboxylate plasticizer provides high flowability and high strength properties. Modification of the structure at the micro level (cementitious matrix level) is an effective means of obtaining superplasticized cementitious systems "Portland cement - fly ash - polycarboxylate superplasticizer". This makes it possible to control the flowability and kinetics of structure formation, to intensify the initial stages of hardening, and to create a particularly strong and monolithic structure of superplasticized cementitious systems for self-compacting concrete.

Prospects for further research

Optimized superplasticized cementitious systems "Portland cement - fly ash - polycarboxylate superplasticizer" are recommended for obtaining eco-self-compacting concretes (Eco-SCC) with a rapid increase in strength on their basis.

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І.І. Кіракевич, Т.С. Кропивницький

Національний університет „Львівська політехніка”,
кафедра будівельного виробництва

ПОВЕДІНКА СУПЕРПЛАСТИФІКОВАНИХ ЦЕМЕНТУЮЧИХ СИСТЕМ ДЛЯ САМОУЩІЛЬНЮВАЛЬНОГО БЕТОНУ

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В статті наведено особливості одержання суперпластифікованих цементуючих систем для самоущільнювальних бетонів з швидким наростанням міцності на їх основі, що поєднують знання закономірностей структуроутворення і модифікування портландцементних композицій „портландцемент – зола винесення – суперпластифікатор” для пошуку раціонального забезпечення заданих будівельно-технічних властивостей бетону.

Досліджено фізико-хімічні особливості процесів гідrataції і тверднення суперпластифікованих цементуючих систем та вирішено проблеми направлено формування мікроструктури цементного каменю. Одержання необхідної швидкості тверднення і щільної структури самоущільнювального бетону досягається за рахунок використання суперпластифікованих в'язучих з наступними ефектами: високою щільністю упакування зерен цементуючої системи за рахунок використання високодисперсних композицій (фізична оптимізація); пуцолановою реакцією при використанні золи виносення (хімічна оптимізація); збільшенням зчеплення між цементною матрицею та заповнювачем (оптимізація мезоструктури бетону).

Результатами досліджень показано, що використання суперпластифікованих цементуючих систем „портландцемент – зола виносення – суперпластифікатор” дозволяє впливати на технологічні властивості та кінетику структуроутворення і створити щільну та міцну мікроструктуру цементуючої матриці бетону. При оптимальному дозуванні зола виносення знижує водопотребу цементної системи і збільшує її рухливість. Це пояснюється тим, що сферичні частинки золи виносення виконують функцію „підшипників кочення”, зменшуючи тертя між частинками. Застосування раціонально підібраних суперпластифікованих цементуючих систем вирішує проблеми одержання швидкотверднучих самоущільнювальних бетонів, що створює можливість використання безвібраційної технології монолітного бетонування конструкцій.

Ключові слова: портландцемент, суперпластифікатор, зола виносення, суперпластифіковані цементуючі системи, самоущільнювальні бетони, швидке наростання міцності.