Possibilities of fly ash utilization in the cement matrix by superabsorbent polymers

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Summary

The paper deals with the possibilities of preparation, processing and basic properties of silicate mass - cement paste using superabsorbent polymer (SAP). SAP is a relatively new additive, which is used in silicate mixtures, where in the early stages of hydration it absorbs excess mixing water and then releases it in the later hydration stages and thus contributes to the elimination of shrinkage cracks. The article deals mainly with the influence of recipe modification with regard to the use of energy by-product of high-temperature fly ash from brown coal combustion and the effects of its use on basic physical and mechanical properties, such as compressive strength, flexural tensile strength and bulk density.

Keywords: *superabsorbent polymer, hydrogel, cement,fly ash.*

Introduction

Superabsorbent polymer (SAP) materials are cross-linked hydrogel networks consisting of water-soluble polymers [1, 2]. SAPs have been utilized in several industries like sanitary, agriculture, and medical [3]. As a type of concrete admixture is application of SAP relatively new [4]. It has been used as an internal curing mechanism to counteract autogenous shrinkage especially in ultra-high performance concrete [5,6,7,8]. SAP can be designed in any shape or size, after its desorption it leaves a void in hardened matrix leading to reduced mechanical properties of cementitious composites [3].

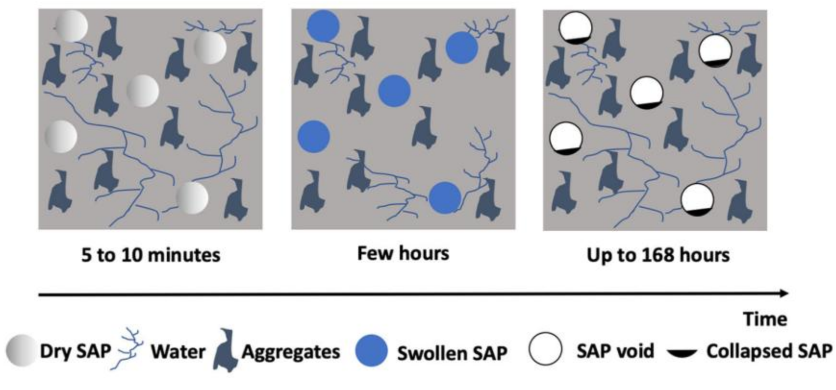

Figure 1: Behaviour of SAP in cementitious paste in different ages [3]

There are various types of SAP based on the source of the material (like natural polymers, synthetic, and semi-synthetic polymers) and production techniques (like radiation cross-linking, network formation, graft, and cross-linking polymerization) [3, 9]. Copolymer of acrylamide and acrylic acid, modified polyacrylamide [10]. These materials are used in ultrahigh performance concrete with cement binder [2,11,12,13,14], into fibre reinforced mortars [10,15,16], composites for cementitious material based on modified metakaolin [17], pavement concrete [5], self-healing and self-sealing cementitious materials [18,19,20,21,22,23], in cement materials in order to determine plastic shrinkage cracking [24,25]

At an early age, the addition of SAP as weak points can reduce the compressive strength of UHPC; however, as age increased, the internal curing water from SAP can densify the microstructure of the vicinity of SAP and compensate the mechanical properties [2]. For practical applications where frost resistance is important, it is necessary to choose a suitable SAP granulometry, which is larger, due to the larger pores, which can be accurately assumed. [26,27]

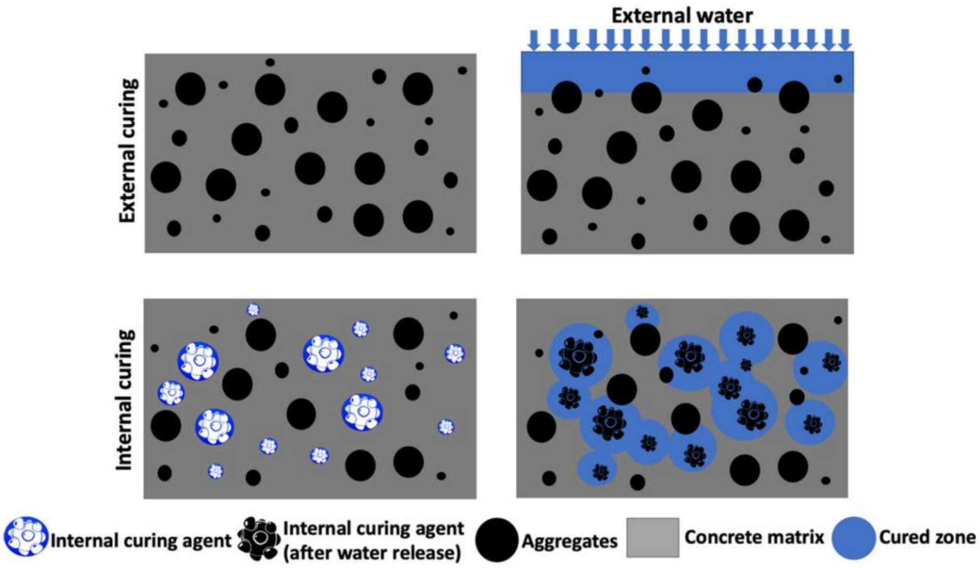

Figure 2: Internal and external curing mechanism [3,27]

Based on the observations of Chindasiriphan and Yokota [28,29], mixtures should have a higher potential for self-healing due to a higher dose of replacement. These are cement mixtures with a high ash content of up to 45% and a high SAP dose of 4%, 6% and 8% by weight of cement. At such high SAP doses, the superabsorbent polymer may absorb most of the water in the mixture. [30] The first use of SAP in real construction, the construction of a pavilion for the FIFA World Cup in Kaiserslautern in 2006, used an amount of SAP of 0.4% by weight of cement with a water content (w/b) of 0.21 and was a sufficient dose to provide concrete up to 45 kg/m^3 of internal curing water. [4]

SAPs are very effective in absorption and desorption, can also be incorporated in dry concrete as an admixture to absorb additional water during mixing [3,31], or it can be used presoaked [32].

Materials

Cement, SAP and as secondary raw materials fly ash were used as input raw materials. Their properties are listed in the tables below.

Cement – CEM I 52.5 R

Powder binder produced in the Hranice cement plant by joint grinding of Portland clinker, calcium sulphate, additional components and additives.

Table 1: Properties of cement

CEM I 52.5 R	***Average values***	***Units***
Compressive strength after 28 days	≥ 52.5	MPa
Specific surface	4 400 – 4 900	cm^2/g
Bulk density	3100	kg/m^3
α	0.64	-

α - expected maximum degree of hydration

Superabsorbent polymer

It is a solid powder in various shapes, based on 2-Propenoicacid, potassium salt (1:1), polymer with 2-propenamide.

Table 2: Properties of superabsorbent polymer CREABLOC SIS

CREABLOC SIS	*Average values*	*Units*
Density	0.7	g/cm^3
Bulk density	720	kg/m^3

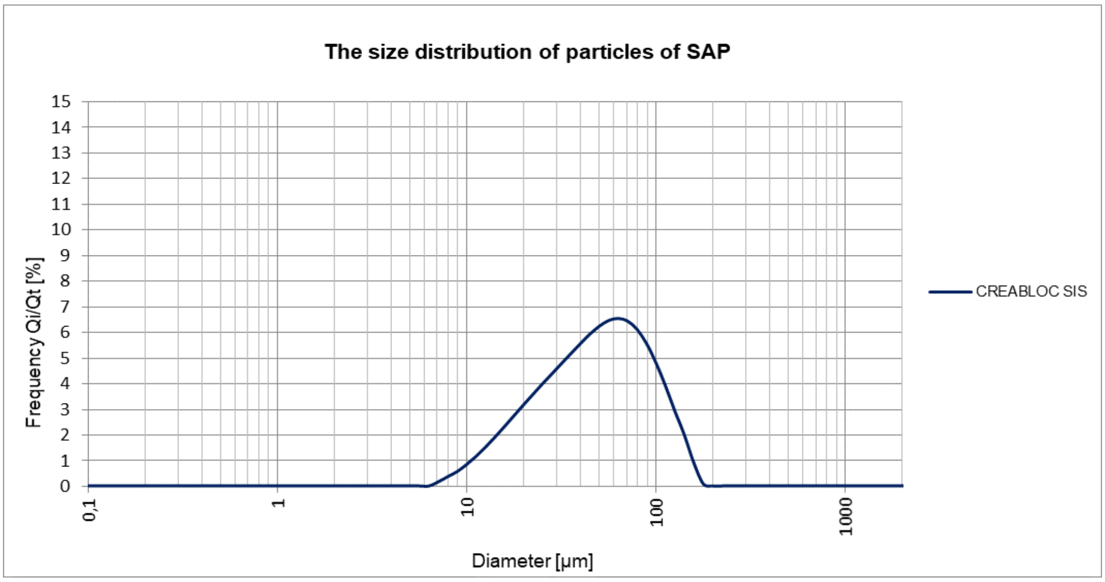

Figure 3: SAP particle size distribution

Fly ash

Used fly ash is a by-product of a brown coal burning thermal power plant in the north middle part of the Czech Republic.

Table 3: Properties of fly ash

Fly Ash - Chvaletice	*Average values*	*Units*
Specific surface	4870	cm^2/g
Bulk density	1150	kg/m^3

Formulations of the mixtures

Mixtures were proposed considering the properties of each input material in order to demonstrate the influence of presence of SAP.

Table 4: Proposed mixture

Mixture	CEM [%]	FA [%]	SAP [%]	w [%]
100 % CEM	100	0	0.00	0.39
90 % CEM + 10 % FA	90	10	0.00	0.40
80 % CEM + 20 % FA	80	20	0.00	0.37
65 % CEM + 35 % FA	65	35	0.00	0.36
100 % CEM + 0.25 % S	100	0	0.25	0.44
90 % CEM + 10 % FA + 0.25 % S	90	10	0.25	0.50
80 % CEM + 20 % FA + 0.25 % S	80	20	0.25	0.48
65 % CEM + 35 % FA + 0.25 % S	65	35	0.25	0.49
100 % CEM + 0.50 % S	100	0	0.50	0.51
90 % CEM + 10 % FA + 0.50 % S	90	10	0.50	0.53
80 % CEM + 20 % FA + 0.50 % S	80	20	0.50	0.55
65 % CEM + 35 % FA + 0.50 % S	65	35	0.50	0.56
100 % CEM + 0.75 % S	100	0	0.75	0.58
90 % CEM + 10 % FA + 0.75 % S	90	10	0.75	0.62
80 % CEM + 20 % FA + 0.75 % S	80	20	0.75	0.63
65 % CEM + 35 % FA + 0.75 % S	65	35	0.75	0.65

Methods

To determine the ideal amount of cement, fly ash and SAP in cement composite, 16 different recipes were proposed. The individual formulations are combinations of fly ash 10%, 20%, 35% and SAP 0.25%, 0.50%, 0.75% (dosing in % by weight of binder).

Mixing was performed in three stages. In the first phase, the loose raw materials were mixed by hand (cement, fly ash) for 2 minutes. In the second phase, a superabsorbent polymer was added to the mixture and mixed by hand for 2 minutes. The resulting bulk mixture had to be completely homogenized in a homogenizer type H2037 - MI800 Mixer Powder Tumbling for 10 minutes at a speed of 910 rpm. In the third (wet) phase, water was added to the completely homogenized mixture so as to achieve the same consistency. The amount of water needed to maintain the consistency of each mixture is recorded in Table 4. The resulting mixture was placed in a mold, the size of each test beam was 40 × 40 × 160 mm.

Consistency was determined in accordance with the standard ČSN EN 1015-3: Methods of test for mortar for masonry - Part 3: Determination of consistency of fresh mortar (by flow table). The ideal spill of the cement slurry was chosen to be 21 × 21 mm.

Bulk density - Determination of the bulk density of hardened mortar (EN 1015-10 - Methods of test for mortar for masonry - Part 10: Determination of dry bulk density of hardened mortar; ČSN EN 196-1: Methods of testing cement - Part 1: Determination of strength).

To determine the compressive strength, a test was performed according to the valid EN 12390-3: Testing of hardened concrete - Part 3: Compressive strength of test specimens and the flexural tensile strength was determined in accordance with EN 12390-5: Testing hardened concrete - Part 5: Flexural tensile strength of test specimens.

Evaluation of the microstructure of the tested materials was performed using scanning electron microscopy. In addition to the study of morphology, an energy-dispersive analysis of the characteristic X-rays was also performed, on the basis of which the chemical composition of selected microscopic subjects was determined.

Results and discussion

On Figure 4 it is possible to see how the strengths change according to the added ash replacement and SAP. With the addition of SAP in an amount of 0.25% of the weight of the cement, the flexural tensile strengths increased with an average amount of added fly ash by 8.8%. Another addition of SAP already had a rather destructive effect on the mixture, and with its further addition, the flexural tensile strength was reduced. The addition of FA in small amounts had a positive effect on flexural tensile strength. Due to the 10% replacement of the FA binder, there was a slight improvement in flexural tensile strength. A higher proportion of FA in the mixture (20% and more) meant a decrease in strength with an increasing proportion of FA.

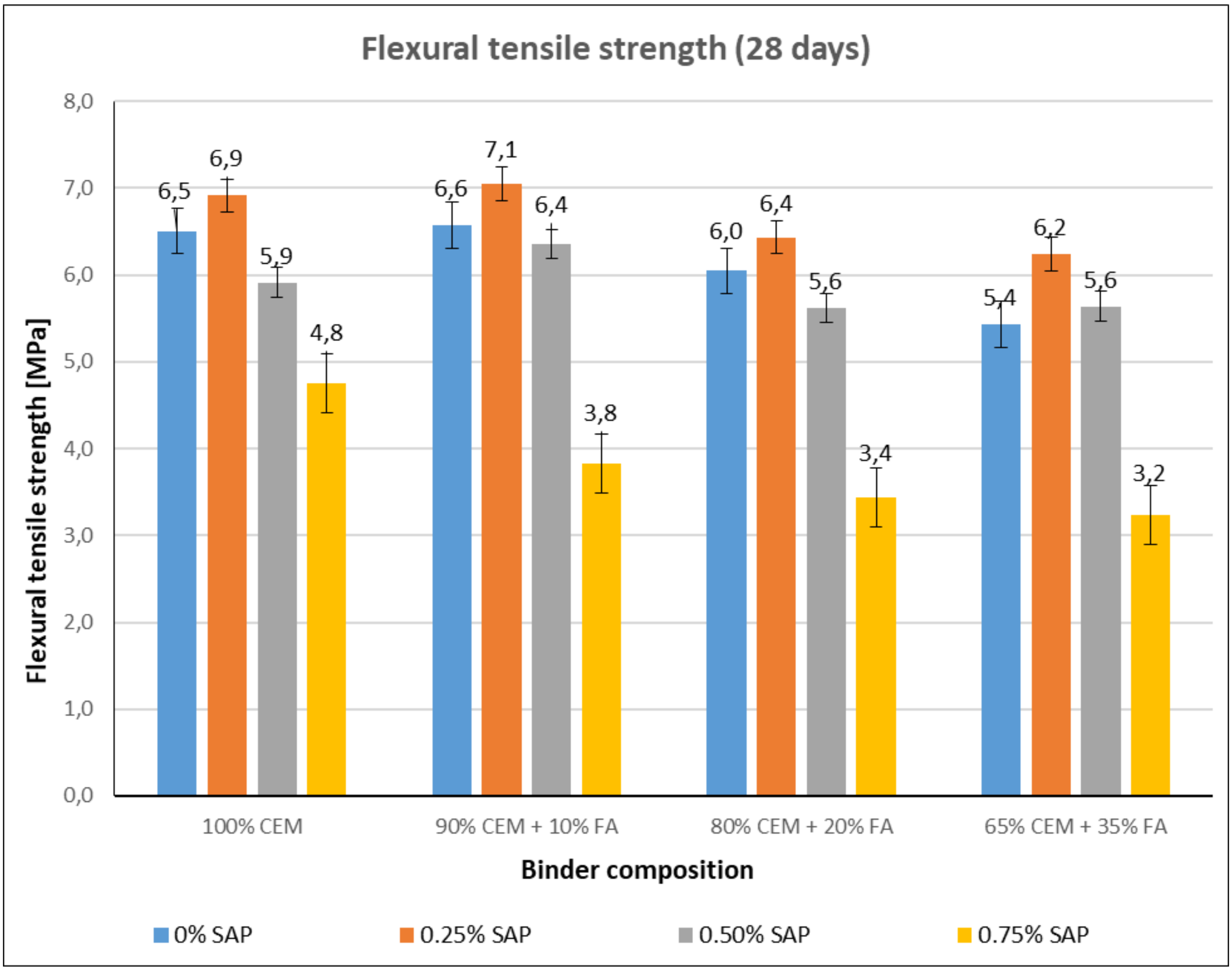

Figure 4: Flexural tensile strength (28 days)

Due to the addition of SAP, there was a slight decrease in compressive strength. Mixtures in which FA was used as a substitute for 10% of the binder component achieved strengths comparable to those in which FA was not contained. With a further increase in the share of FA and SAP, there was a decrease in compressive strength. The exception was the mixture with 20% FA binder replacement and 0.25% SAP, in which the decrease in compressive strength was not very significant compared to the reference mixture.

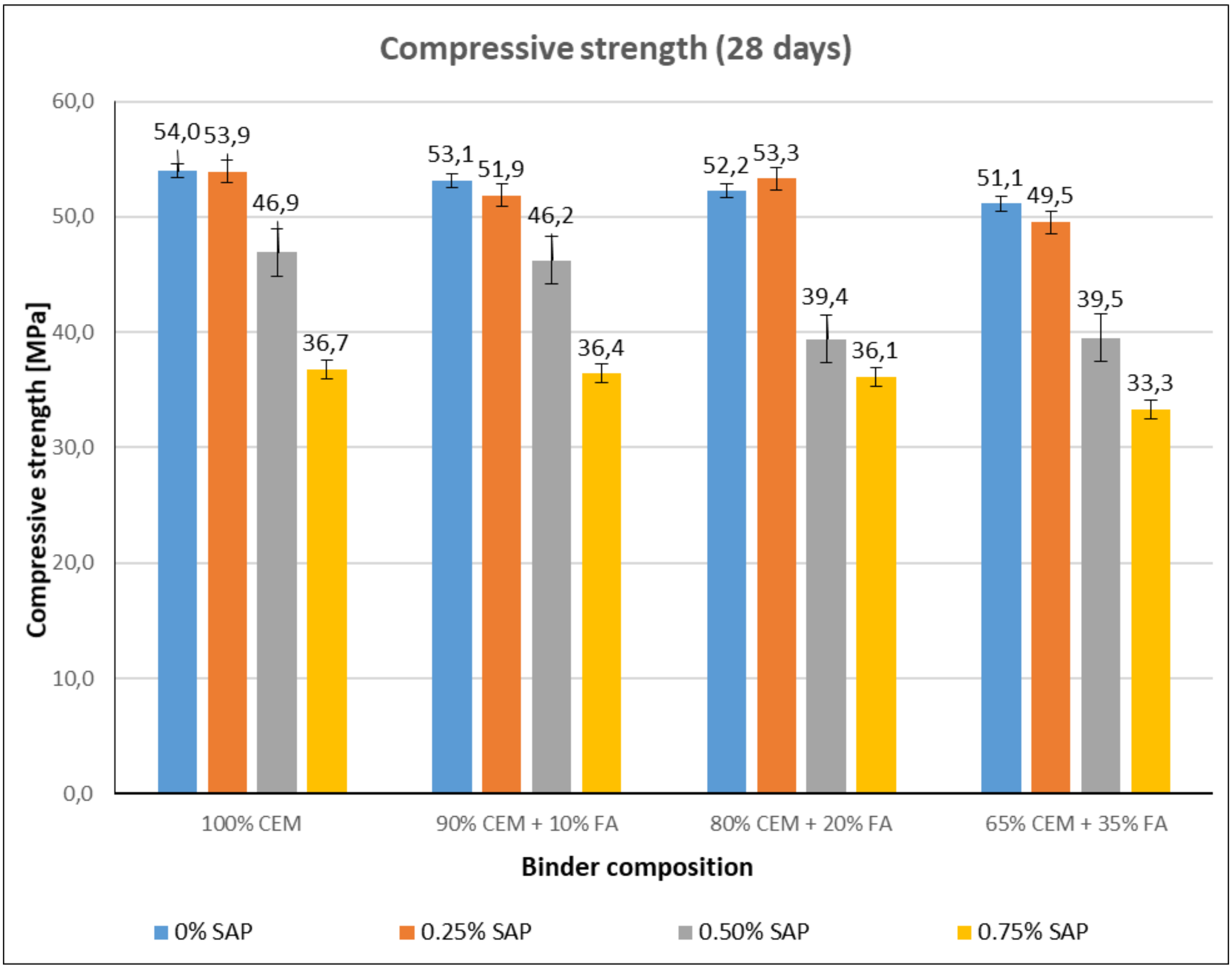

Figure 5: Compressive strength (28 days)

From the comparison of the bulk density of individual mixtures, it is evident that with the increasing share of the replaced binder component by FA, the bulk density decreases. It is also clear that as the amount of SAP used increases, the bulk density of the samples also decreases.

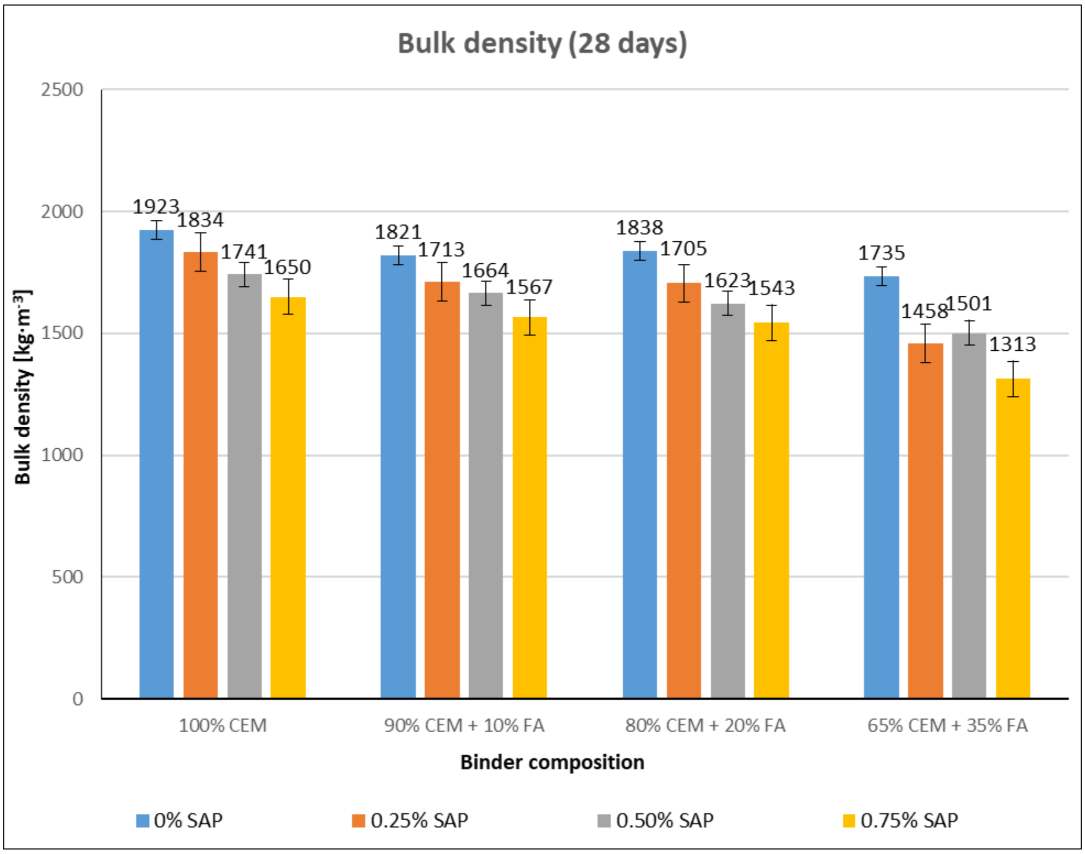

Figure 6: Bulk density (28 days)

Typical features detected by scanning electron microscopy are captured in the following images:

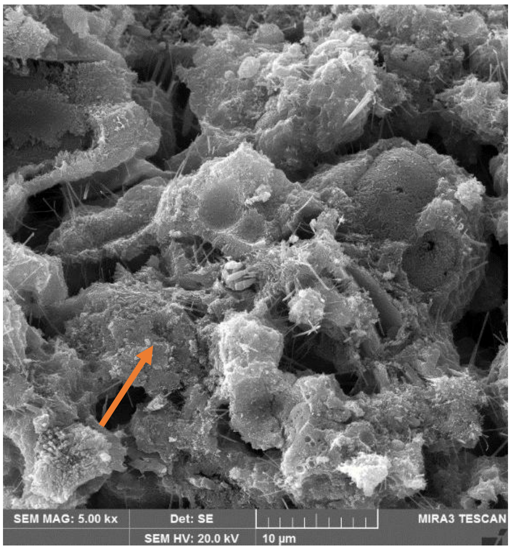

Figure 7: View of the mixture with 35% fly ash without SAP

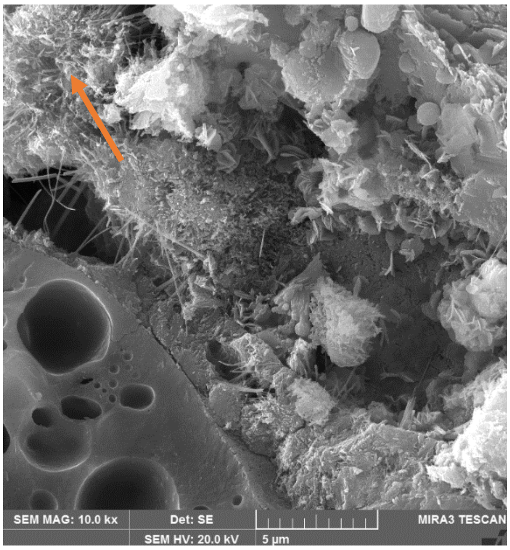

Figure 8: Detailed view of the contact zone of the cement matrix and fly ash grains in a composite with 35% cement substitution by fly ash, without SAP

On Figure 7 is a microstructure typical of cement fly ash composites. The presence of cement hydration products (especially calcium hydrosilicate gels), which surround the ash grains, is evident. (magnified 5,000 times). On Figure 8 presence of calcium hydrosilicate gels and prismatic crystals of primary ettringite is evident. (magnified 10,000 times).

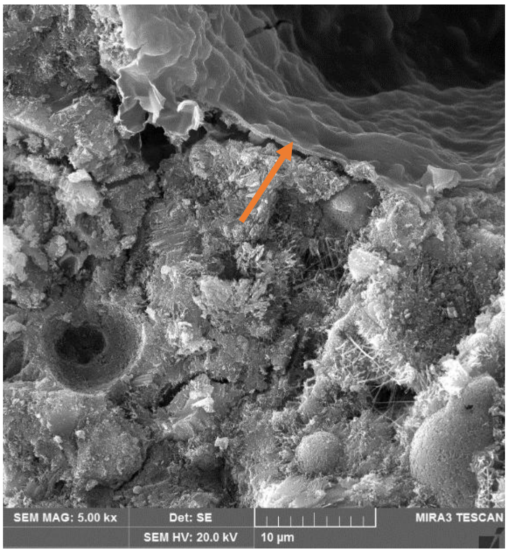

Figure 9: View of one of the pores in the microstructure of a composite with 35% fly ash and 0.75% SAP

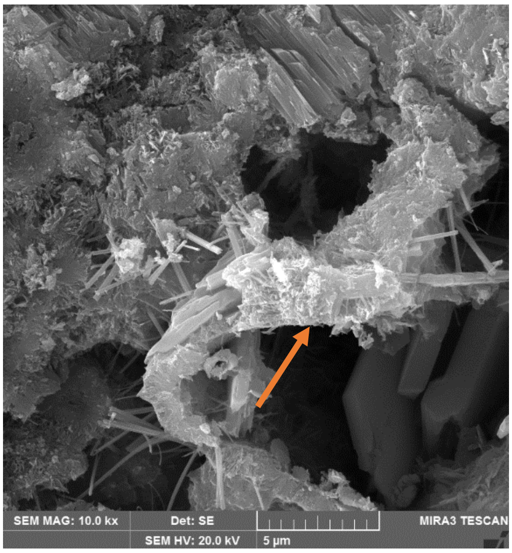

Figure 10: Detailed view of a polymer film in one of the pores of a composite with 35% fly ash and 0.75% SAP, indicated by an arrow

On Figure 9 a "coating" of organic polymer on the wall of one of the pores is indicated, indicated by an arrow (magnified 5,000 times). On Figure 10 the druses of portlandite are also noticeable. (magnified 10,000 times).

One of the essential findings of electron microscopy is a clear demonstration of the formation of a "coating" or. film of organic material (the SAP used is predominantly formed by organic substances) on the walls of some pores, at a dose of SAP 0.50%, and especially at a dose of 0.75%. The formation of this "coating" indicates a de facto redundant amount of SAP in the mixture at these doses. Furthermore, it has been shown that the mixtures with higher doses of SAP have a relatively lower portlandite content. This finding probably indicates the ability of SAP to bind calcium ions released by the gradual hydration of cement, which was confirmed by determining the chemical composition of the "coating" in the pores.

Conclusions

The article is focused on the optimization of the dose of superabsorbent polymer in connection with the possibility of substituting cement with power plant fly ash in such modified composites.

It was stated that while the substitution of cement with fly ash affects the rheology of the fresh mixture to a very limited extent, the SAP admixture significantly increases the requirements for the mixing water dose when the comparable workability of the fresh mixture is required. This is particularly striking at higher doses of SAP, for example at a dose of 0.75%, the dose of mixing water was increased by more than half to maintain the consistency of the fresh mixture. From the obtained results it is apparent that the utilization of fly ash in cement matrix by usage of superabsorbent polymers is possible. Concretely by improving final properties of mixtures containing these secondary raw materials. Especially flexural tensile strength was increased by the addition of SAP in various amounts compared to the reference samples at substitution rate of binder by FA 10%. At the substitution rate by FA 20% and higher meant decrease in flexular strength, but nevertheless the addition of 0.25% of SAP still increased the values compared to the reference samples. Compared to the reference samples the compressive strength was increased only by addition of 0.25% of SAP at the substitution rate of binder by FA at the rate of 20%. Considering the bulk density, it is apparent that the increasing share of FA as well as increasing content of SAP in samples both decrease the values of obtained bulk density of the mixtures. Only exception is slight increase of bulk density of mixture 65% CEM + 35% FA with 0,50% SAP compared to mixture with 0,25% SAP. This fact might have been caused by the bigger deviation in measurements of mixture with 0,25% SAP, which can be observed in its error line.

The analysis of the microstructure revealed that SAP is very likely to enter into matrix formation reactions, being able to bind calcium ions released by cement hydration into its structure.

List of symbols

SAP – superabsorbent polymer,
CEM – cement (CEM I 52,5 R),
FA – fly ash.

Acknownledgments

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Možnosti využití popílku v cementové matrici se superabsorpčními polymery

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Souhrn

Příspěvek se zabývá možnostmi přípravy, zpracování a základními vlastnostmi silikátové hmoty – cementové pasty s využitím superabsorpčního polymeru (SAPu). SAP je poměrně novou přísadou, která se používá v silikátových směsích, kde v raných fázích hydratace absorbuje přebytečnou záměsovou vodu a tu následně uvolňuje v pozdějších hydratačních stadiích a přispívá tak k eliminaci smršťovacích trhlin. Článek se zabývá zejména vlivem úpravy receptur s ohledem na využití vedlejšího energetické produktu vysokoteplotního popílku ze spalování hnědého uhlí a dopady jeho využití na základní fyzikálně mechanické vlastnosti, jako jsou především pevnost v tlaku, pevnost v tahu za ohybu a objemovou hmotnost.

Klíčová slova: *superabsorpční polymer, hydrogel, cement, popílek.*