POSSIBILITY OF THE MODIFICATION OF THE PROPERTIES OF SULFOALUMINATE BELITE CEMENT BY ITS BLENDING

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The results obtained showed the possibility of the blending of sulfoaluminate belite (SAB) cement by mineral admixtures, like fly ash, silica fume, and basic blast furnace slag when reaching satisfied engineering properties of the blend. The optimum of the addition of the mineral admixture in the SAB cement blends representing the value ca 15 wt.% is significantly lower than the optimum at Portland cement blends with values between 20 to 40 wt.%. This is caused by the decreased production of calcium hydroxide during SAB cement hydration. It has been found that the blending practically did not influence settings. On the contrary, very well known strength decrease by the blending opposite to the original SAB cement was observed. This strength decrease of the studied blends represents the values between 5-20 % depending on the kind of the admixture and its quantity in the blend.

INTRODUCTION

Blending of Portland cement by means of pozzolanic materials like dacite tuff, fly ash, silica fume and slag gives the possibility of the modification of its properties and concretes prepared from blends. Important effects, which can be reach, are decrease in hydration heat, improved workability of fresh concrete mixtures, volume stability, water tightness, improved chemical resistance in some aggressive media, ultimate strength increase, and other improved engineering properties of concretes.

Pozzolans are powdered vitreous pyroclastic materials formed by violent volcanic action or in high temperatures technologies as the combustion of coal or in iron production. That is why the pozzolans contain amorphous glassy phase, which allows in presence of humidity or water at normal temperature to react with calcium hydroxide to form calcium silicate hydrates similar to those found in the hydration of Portland cement. The calcium hydroxide needed for pozzolanic reaction is produced during the hydration of belite and mainly alite [1]. Therefore the extent of pozzolanic reaction and its effects on the properties of the blend is affected by the content of both phases in Portland cement. The belite is a unique source of calcium hydroxide production at SAB cements. Owing to the composition of belite, having lower calcium oxide content comparing to alite, the production of calcium hydroxide during hydration of sulfoaluminate belite cements is significantly decreased. Therefore, the lower optimal portions of pozzolans added can be expected at sulfoaluminate belite cement blends opposite to those of Portland cement for which the optimal portions of pozzolans occur between 20 to 40 wt.%. Till now a small attention has been paid to the blending of belite cements, especially sulfoaluminate belite cements. Mikoc and Malkovic prepared blended belite cements with 20 to 30 wt.% of silica fume [2]. The blended belite cements are produced commercially using high belite clinkers in

India [3]. This shows the possibility of the blending of sulfoaluminate belite cements. However the optimal addition for the given cement and pozzolan should be ascertained experimentally.

The SAB cement as a result of a COPERNICUS project [4] was developed using the results of basic and technological research [5, 6].

The paper presents the result of the study of the possibilities of sulfoaluminate belite cement blending and the optimal portioning of pozzolans like fly ash, granulated slag and silica fume.

EXPERIMENTAL PART

The pastes used for the study were made from sulfoaluminate belite cement blends containing 5, 15 and 30 wt.% of basic granulated blast furnace slag, fly ash, and silica fume. The original sulfoaluminate belite cement was prepared as a reference sample. Sulfoaluminate belite cement was synthesised by heating in an electric furnace at 1250 °C using mixture of limestone, gypsum, fly ash and pyrite ash. Chemical composition and properties of material used are listed in table 1.

The prepared pastes were homogenised to have constant consistency. The values of water to cement ratio (*w*/*c*) are given in table 2. It can be seen that only at the silica fume blends it was needed to increase *w*/*c* values significantly.

Consistency, initial of setting and time of setting were tested by Vicat apparatus according to standard

Table 1. Chemical composition and properties of materials used.

Composition (wt.%) and properties	Material			
	sulfoaluminate belite cement	granulated basic blast furnace slag	fly ash	silica fume
humidity	0.10	1.70	1.19	0.40
ignition loss	0.48	2.01	1.95	1.34
ins. residue	1.35	0.79	-	-
SiO_2	19.69	36.91	54.04	97.07
Al_2O_3	15.45	8.05	22.84	0.21 (R_2O_3)
Fe_2O_3	2.60	0.60	6.06	-
CaO	52.58	40.47	7.65	0.54
MgO	1.50	9.00	1.77	0.40
SO_3	6.12	0.60	1.29	-
specific weight (kg m^{-3})	3007.7	2952.3	2075.2	2268.7
spec. surface area (m^2 kg^{-1})	381.3	408.8	350.2	15 897.6 (BET)
initial of setting	10 min	-		-
time of setting	30 min	-		-
mineralogicalcomposition (wt.%) (calculated)	C_2S 53.2 $C_4A_3\bar{S}$ 33.9 C_4AF 7.9 $CaSO_4$ 4.3			

Table 2. Values of water: cement ratio and setting characteristics.

Composition of binder		water to cement ratio	setting	
SAB (wt.%)	pozzolan (wt.%)		initial of setting	time of setting
100	-	0.34	1 hr 10 min	3 hrs 20 min
	slag			
95	5	0.34	1 hr 15 min	3 hrs 30 min
85	15	0.33	1 hr	2 hrs 45 min
70	30	0.33	1 hr	3 hrs
	fly ash			
95	5	0.34	1 hr 10 min	2 hrs 50 min
85	15	0.35	55 min	2 hrs 30 min
70	30	0.38	50 min	2 hrs 10 min
	silica fume			
95	5	0.32	27 min	1 hr 10 min
85	15	0.34	27 min	1 hr 5 min
70	30	0.41	32 min	1 hr 20 min

STN 722 115. The constant consistency of the prepared cement pastes was expressed by the value of 5 - 7 mm of distance between the bottom of Vicat cylinder and the paste specimen. Then, compressive strength of the hardened cement pastes was estimated after 1 and 28 days of hardening. The 20 mm - edge cubes, were cured 24 hrs at 95 % humidity and 27 days in water at ambient temperature of 20 ± 2 °C. Thermal analysis equipment enabling DTA and GTA data was used (Thermal analysis programme T.A.Instruments) for estimation of calcium hydroxide content in cement pastes.

Pore structure of the hardened cement pastes was studied by means of mercury porosimetry, when the microporosimeter mod.2000 and macroporosimeter unit

120 ERBA SCIENCE were used. For the calculation of the results, following parameters was used: wetting angle of 141.3° and surface tension of 0.48 N m^{-1}. The possible estimated pore radius varied from 3.75 nm to 0.3 mm. The values of water permeability coefficient were calculated using the results of porosimentry by means of the method developed in our laboratory [7].

RESULTS AND DISCUSSION

The results of setting test are given in table 2. It can be seen that blending by slag and fly ash had practically a negligible influence on the initial of setting of the pastes. But blending by silica fume decreased the initial of setting by ca 50 % opposite to slag, and fly ash blends and original sulafoaluminate belite cement. The same relationships could be observed at values of setting time. It means again minimal influence of slag and fly ash on setting time of the related pastes, but a significant shortening of setting time of silica fume blends with the values of ca 60 - 70 %. It is evident that silica fume by its effect on setting characteristics of blend differ entirely opposite to the effects of slag and fly ash.

Figure 1 shows that addition of the studied pozzolans to the sulfoaluminate belite cement caused a decrease in compressive strength of the pastes after 1 and 28 days of hardening. This effect of the blending is very vell known at the Portland cement [1, 8]. Therefore, the compressive strength decrease is not a special effect of the blending of sulfoaluminate belite cements. As it can be seen in figure 1, the pastes prepared from blends of 5 wt.% fly ash and silica fume show ca 20 % increase in compressive strength opposite to the original sulfoaluminate belite cement paste - after 28 day of hardening. Probably a higher pozzolanic activity of fly ash and silica fume opposite to that of slag caused the observed different effect on compressive strength development.

The pozzolanic activity was evaluated using estimated value of constant a of curve of heat liberation rate. The method of dissolution heat (MDH) is based on the estimation of the kinetics of the evolution of dissolution heat of the tested material. This can be expressed by the equation:

$$DH = \frac{1}{a + bt} \qquad (1)$$

where *DH* is dissolution heat in the given time *t*, *a* and *b* are constants.

Another characteristic of pozzolanic activity is the ratio of heat liberated (*HR*) after 5 and 60 min of the action of diluted solution of HNO_3 on the tested pozzolan. In addition, samples were evaluated by insoluble residue content in the pozzolan or its content in active components respectively.

The characteristics of pozolanic activity gained by means of MDH for some pozzolans are listed in table 3.

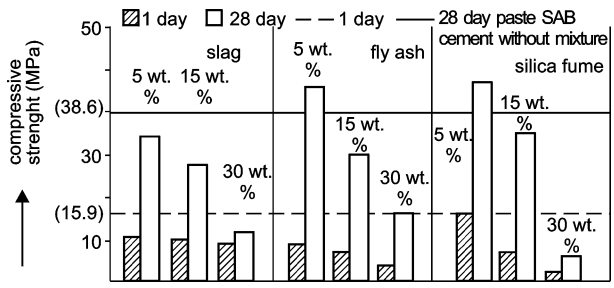

Figure 1. Dependence of compressive strength of sulfoaluminate belite cement blend pastes on the kind, portion of pozzolan added and time of hardening.

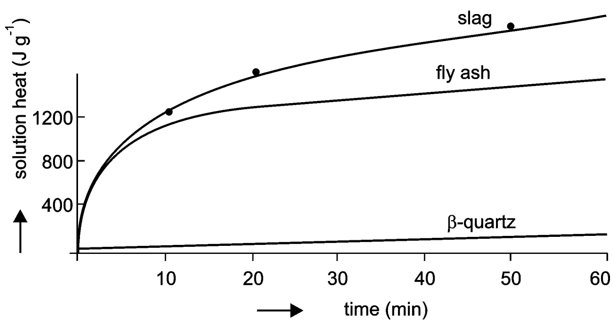

Figure 2. Evolution of solution heat of some pozzolans [9].

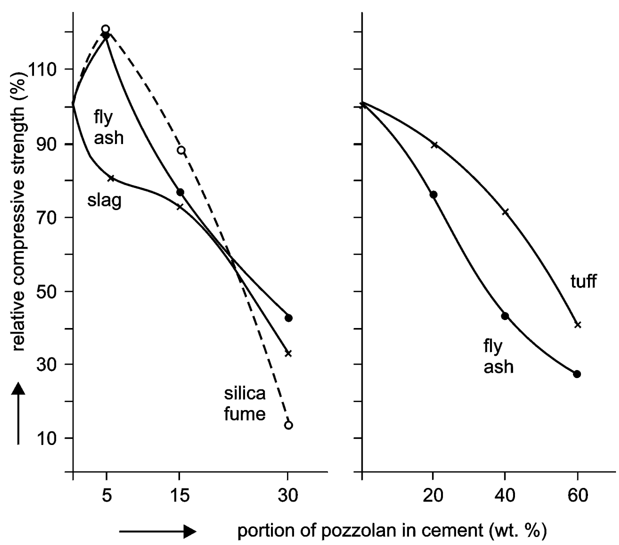

Figure 3. Comparison of the effect of the blending of sulfoaluminate belite and Portland cements on the values of compressive strength of hardened pastes, data on Portland cement blends [10].

Evolution of solution heat of some pozzolans is shown in figure 2. These results are reported in the paper [9].

The activity of the pozzolan is increased with the decreasing values of constant a and with the increasing values of *HR*. These relations are very well documented

Table 3. Parameters of activity for some materials estimated by means of MDH [9].

Characteristics of pozzolanic activity				
material	insoluble residue (wt.%)	dissolution heat ($J g^{-1}h^{-1}$)	constant (a 10^{-7})	ratio of dissolution heat 5 : 60 min
Basic blast furnace slag	17.8	2002	34834	0.452
fly ash	24.2	1658	78854	0.638
dacite tuff	13.2	1591	20810	0.889
β - quartz	95.3	88	5151000	0.369

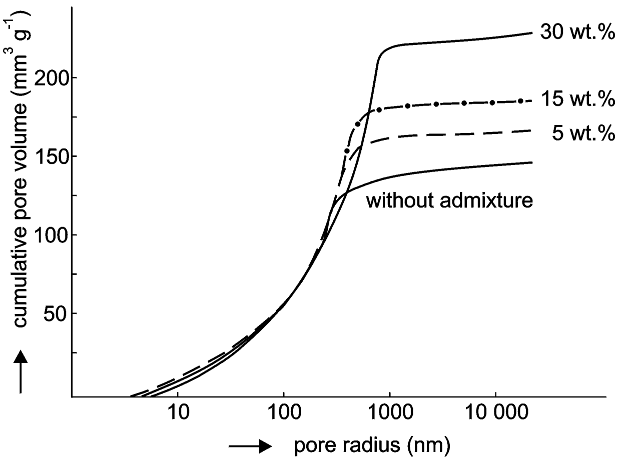

Figure 4. Curves of pore radius distribution in the pastes prepared from the blends of sulfoaluminate belite cement and fly ash after 28 days of hardening.

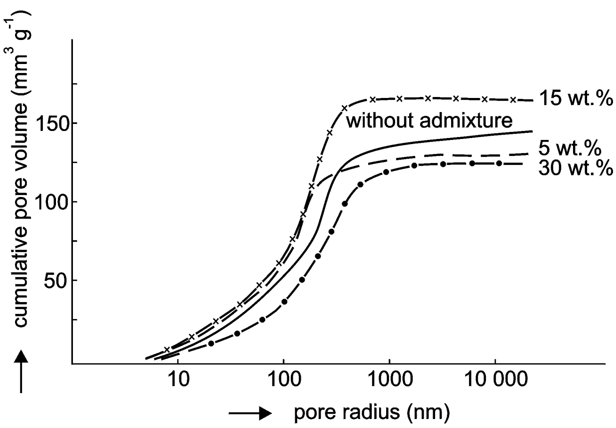

Figure 6. Curves of pore radius distribution in the pastes prepared from the blends of sulfoaluminate belite cement and silica fume after 28 days of hardening.

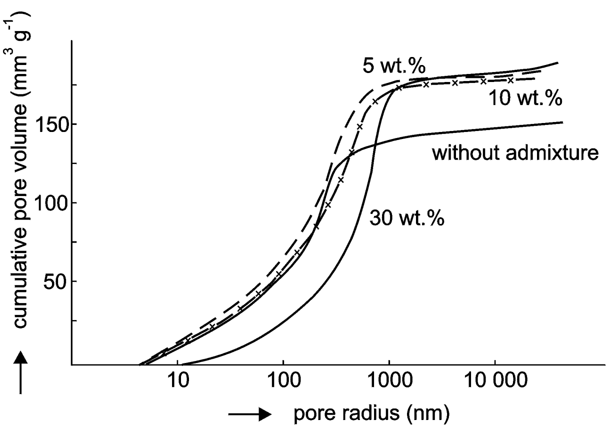

Figure 5. Curves of pore radius distribution in the pastes prepared from the blends of sulfoaluminate belite cement and slag after 28 days of hardening.

by the values of β - quartz. It can be seen that at this material, acting as an inactive substance, the values of constant a and *HR* reach extreme maximal and minimal values. On the other side, dacite tuff seems to be the most active among the studied pozzolans with the lowest value of insoluble residue and constant a, and the highest value of *HR*. This corresponds with the highest compressive strength values reached by tuff Portland cement blends (figure 3). According to the parameters of pozzolanic activity and the effect on compressive strength, fly ash and slag seem to be practically equivalent pozzolans when applicated in sulfoaluminate belite cement blends (figure 1). But, fly ash at the portions 5 and 15 wt.% in these blends is more active pozzolan than slag. This is evident when comparing the effect of pozzolans on the compressive strength of the related hardened pastes.

Table 4 shows the results of the study of pore structure of cement pastes after 28 days of their hardening. Curves of pore radius distribution are shown in figures 4, 5 and 6. A realistic parameter of pore characteristic is pore radius median. Dependence of compressive strength on pore radius median is shown in figure 7. Figure 8 shows the dependence of coefficient of water permeability on pore radius median. In addition, other engineering properties like watertightness, chemical and frost resistance of cement-based materials are dependent on pore size.

It can be seen that dosage of 30 wt.% pozzolans caused a significant increase in the values of pore volume, pore median, total porosity, and coefficient of water permeability opposite to those reached by lower dosages of 5 and 15 wt.%. It documents a significant decrease in the quality (pore volume and pore median

Table 4. Pore structure characteristics of cement pastes after 28 days of hardening.

Composition of blend		Pore structure characteristics					
admixture	(wt.%)	pore volume (mm^3 g^{-1})	pore median (nm)	macropore (r > 7500 nm) fraction (%)	total porosity (%)	specific surface area (m^2 g^{-1})	coefficient of water permeability (K × 10^{-10} m^{-1})
		185	163	2.7	31.6	8.6	105.0
slag	15	185	182	3.1	32.9	8.6	145.2
	30	192	485	4.7	31.5	2.4	609.1
	5	177	173	3.0	29.2	7.9	110.8
fly ash	15	194	205	2.8	32.6	7.7	179.4
	30	239	314	4.3	36.6	7.8	350.4
	5	139	97	2.4	24.6	8.5	29.6
silica	15	173	115	1.1	30.2	9.3	63.9
fume	30	265	156	1.8	38.1	11.3	150.9
SAB cement	-	155	154	5.4	27.2	6.4	73.6

Table 5. Results of gravimetric thermal analysis of cement pastes after 28 days of their hardening.

Composition of blend	Ignition loss (wt.%)				
admixture	(wt.%)	water bound 100-420 °C	$Ca(OH)_2$ 420-580 °C	calcite 580-700 °C	total
	5	10.0	1.2	0.6	13.0
Slag	15	8.2	1.0	1.0	11.2
	30	7.7	0.7	1.0	10.7
	5	8.1	1.9	0.4	13.1
fly ash	15	8.2	1.1	0.7	11.5
	30	6.2	0.6	0.6	8.8
	5	8.7	1.0	0.6	11.6
silica fume	15	7.2	1.2	0.3	10.2
	30	6.4	1.4	0.3	9.2
SAB cement	0	10.6	1.2	0.8	13.9

increase) of the formatted pore structure with increasing dosage of pozzolans over 15 wt.%. Evidently, it was a consequence of a overcoming the proper ratio between the quantities of cement and pozzolan in the blend. This ratio is affected by the activity of pozzolan and quantity of calcium hydroxide liberated during hydration of cement in the blend. Then, overcoming quantity of pozzolan added does not enter pozzolanic reaction owing of the lack of calcium hydroxide and it can act only as a filler. This fact brings a drastic compressive strength decrease, which can be seen in figure 1.

Results summarised in table 4 indicate that the silica fume addition has effect that is more beneficial at dosage 5 and 15 wt.% as a consequence of its high silica content and a degree of dispersity comparing those of fly ash and slag.

The results show that satisfactory properties of hardened pastes prepared from SAB blends are reached at the dosages of pozzolans 15 to 20 wt.%. An elevated addition 30 wt.% of pozzolan resulted in a significant increase in pore sizes.

A significant factor of the extent of pozzolanic reaction in the blends is the amount of calcium hydroxide liberated in hydration of their cement component. Owing to the significant difference in the mineralogical composition it brings decreased quantity

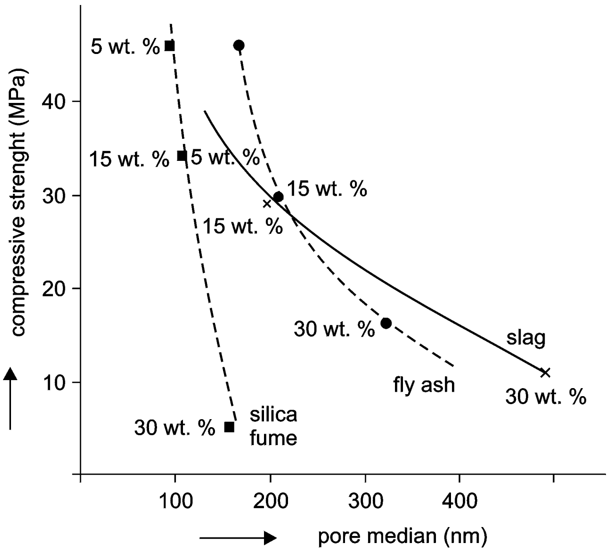

Figure 7. Relationship between pore median and compressive strength of the pastes prepared from sulfoaluminate belite cement blends after 28 days of hardening.

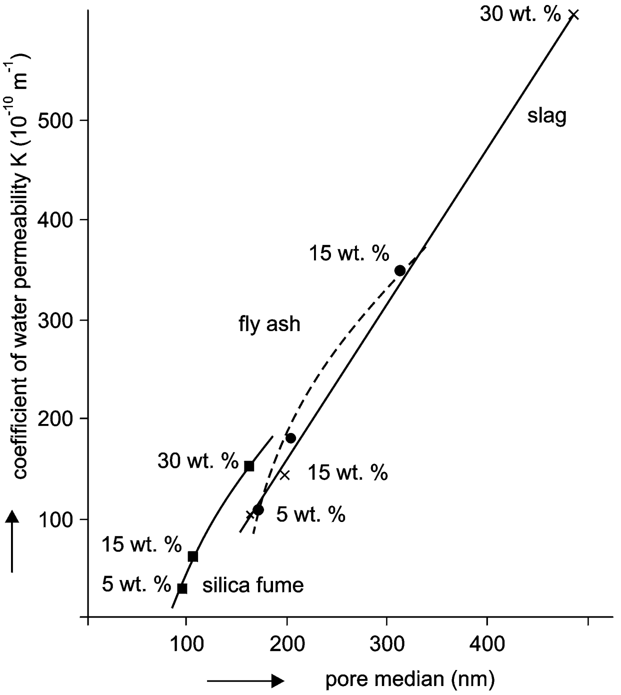

Figure 8. Relationship between pore median and coefficient of water permeability of the pastes prepared from sulfoaluminate belite cement blends after 28 days of hardening.

of calcium hydroxide liberated in the hydration of sulfoaluminate belite cements opposite to that liberated in hydration of Portland cement.

Figure 9 indicates difference between phase composition of both SAB and Portland hardened cement pastes. Portland cement hardened paste exhibits

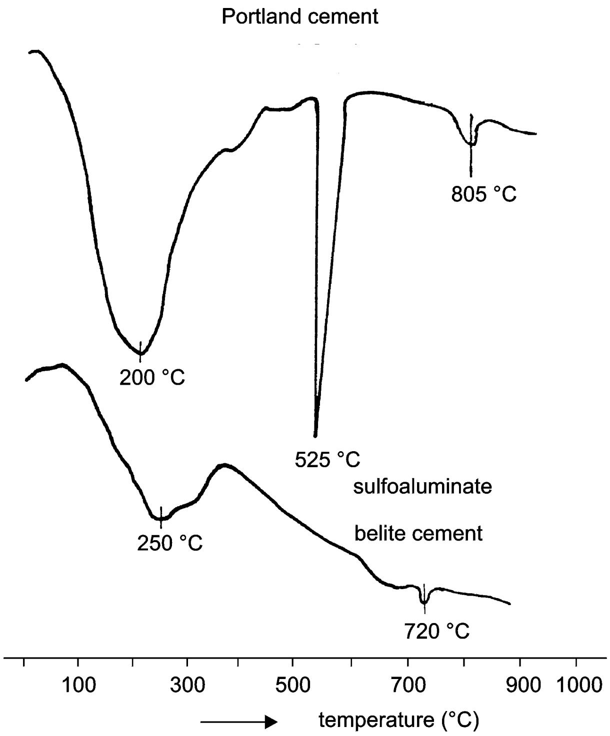

Figure 9. DTA curves of Portland cement and sulfoaluminate belite cement pastes after 28 days of hardening.

on DTA curve endothermic peak at 200 °C corresponding to the dehydration of calcium silicate, calcium aluminate hydrates and related SO_3 containing compounds. The minima at 525 and 805 °C belong to the dehydration of calcium hydroxide and decomposition of its carbonation product calcite. Small endothermic peak at 250 °C belonging to the dehydration of calcium silicate hydrates, ettringite and hydration products of C_4AF can be seen on DTA curve of sulfoaluminate belite cement hardened paste. In addition, small endothermic peak indicating the decomposition of calcite takes place at 720 °C. However, no peak belonging to the dehydration of calcium hydroxide was observed.

DTA curves of the hardened blend pastes had similar character. No significant changes depending on the kind and quantity of pozzolans added were observed. In accordance with DTA analysis results the results of GTA (table 5) show only minimal changes in bound water and the ignition loss content corresponding to the dehydratation of calcium hydroxide and decomposition of calcite.

It was impossible to determine if a moderate decrease in ignition loss with an increase of pozzolanic addition was caused by the development of pozzolanic reaction with consumption of calcium hydroxide or by a decrease in cement content in the blend

It is clear that content of calcium hydroxide liberated in sulfoaluminate belite cement hydration is significantly decreased opposite to that liberated in

Portland cement hydration. Therefore, the quantity of calcium hydroxide for pozzolanic reaction in sulfoaluminate belite cement blends is naturally significantly decreased. It represents decreased possibility for well - found portions of pozzolans in these blends opposite to Portland cement blends. This fact is shown in figure 3. The mineralogical composition of the cements used was (wt.%): Portland cement C_3S 46.1, C_2S 29.2, C_3A 7.0, C_4AF 12.0; SAB cement C_2S 53.2, $C_4A\overline{S}$ 33.9, C_4AF 7.9 CS 4.8. It can be seen that it was possible to add the higher portions of pozzolans into Portland cement blends than sulfoaluminate belite cement ones. It is evident when the compressive strength values in dependence on pozzolan portioning are compared. Optimally ca 20 to 40 wt.% versus ca 5 to 15 wt.%, when proper compressive strength, and other important engineering properties of concretes made from sulfoaluminate belite cement blends should be reached.

CONCLUSION

1. The results showed the principal possibility to blend the sulfoaluminate belite cements by means of pozzolans. It makes possible a disposal of solid industrial waste having pozzolanic character. Beside the aimed modification of the properties of sulfoaluminate belite cements by blending this can bring a positive environmental effect.
2. An important and unavoidable factor of pozzolanic reaction, which is a basic principle of resulted effects of the blending, is the quantity of calcium hydroxide liberated in the hydration of sulfoaluminate belite cement in the blend. This quantity is relative low opposite to Portland cement. As unique source of calcium hydroxide is the hydration only of β-C_2S, the optimal portions of pozzolans in the SAB blends is 5 to 15 wt.% versus 20 to 40 wt.% in Portland cement blends.
3. The effect of blending of sulfoaluminate belite cements depends on the activity of pozzolans and properties of the cement used, mainly on its content of β-C_2S. Both activity of pozzolan and properties of the cement are very complex. Therefore, the tests of the mixtures of sulfoaluminate belite cement with the graduated portions of pozzolans seem to be the most convenient and reliable way for the determination of the optimal composition of the blends for the ensuring the demanded engineering properties of concrete. Therefore, verification tests are needed.

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Submitted in English by the author.

MOŽNOSTI MODIFIKÁCIE VLASTNOSTÍ SULFOALUMINÁTOVÉHO BELITICKÉHO CEMENTU PRIDANÍM PUZOLÁNOV

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Predmetom výskumu bola možnosť prípravy zmesného sulfoaluminátového belitického cementu za použitia popolčeka, kremičitého úletu a granulovanej zásaditej trosky. Výsledky preukázali možnosť úpravy vlastností cementu a materiálov z neho vyrobených. Podľa výsledkov optimálne dávkovanie v zmesnom sulfoaluminátovom belitickom cemente sa pohybuje v rozsahu ca 5 až 15 % z hmotnosti cementu. Jedná sa o dávky podstatne nižšie oproti zmesným portlandským cementom s optimálnym dávkovaním prímesí 20 až 40 %. Ukázalo sa, že je to dôsledok zníženej produkcie $Ca(OH)_2$ pri hydratácii sulfoaluminátového belitického cementu.