EVOLUTION OF LIGHTWEIGHT FOAM CONCRETES BY WATER PROCEDURE

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The so called water procedure was used to prepare foam concrete samples with bulk density below 150 kg·m^{-3}. Direct foaming method was applied by using of protein based foaming agent. The amount of Portland cement was decreased gradually along with the water-cement ratio maintenance. Degradation of foams occurred with reducing of cement content to 30 % of its original quantity regardless of water procedure included or not in the preparation procedure. Stability of the foam concrete samples prepared only from 30 % of cement was achieved after microwave and ultrasonic treatment of protein based foaming agent. The so prepared foam concretes were stable also after water procedure and exhibited final bulk density of 95 kg·m^{-3}.

INTRODUCTION

Water procedure as a way to produce very porous material was for the first time reported by Pach et al [1]. This adaptation of usual direct foaming method served the authors to prepare stable alumina foam with bulk density of 50 kg·m^{-3} and porosity of 99 %. Dilution of the foams with water resulted in the separation of particles which were not physically bond in lamellas. As a result, lamellas got thinner and pores arranged in the ideal polyhedral positions.

The aim of the present study is to exhibit that mentioned water procedure is adaptable also for preparation of foam concretes. It will be proved that by using of this adaptation of conventional direct foaming method it is able to prepare foam concretes with very low bulk density and in this way extend the application possibilities of this kind of materials.

In order to reduce final bulk density of samples as much as possible, cement content was gradually lowered. After reaching the minimum value of cement amount under the given conditions, treatment of protein foaming agent was examined to overcome this border by improvement of foaming agent effectivity.

As we have demonstrated in our previous study [2], stability and foaming efficiency of the protein based foaming agent can be improved by its microwave and ultrasonic treatment. The same procedure of foaming agent treatment was therefore used in the cases where reducing of cement content caused the degradation of the foams.

Positive effect of ultrasound on the surface chemistry of proteins is mainly attributed to the acoustic cavitation which occurs at frequencies of ultrasound up to 2.5 MHz and causes the following: (a) extremely increase of local temperatures, which result in increased solubility and diffusivity (b) large shear forces and jetting which favor penetration and transport at liquid/liquid or liquid/solid matrix and (c) the formation of highly oxidizing radicals during sonolysis of the solvent (hydroxyl and hydrogen peroxide for water) [3, 4].

Microwave heating causes the denaturation of proteins, i.e. violation of their quaternary, tertiary and secondary structures whereby their primary structure remains unchanged [3, 5]. Denaturation of proteins could expose hydrophobic regions which are necessary for adsorption of molecules on the air/water interface. Foaming stability depends on the duration of microwave treatment which determines denaturation level [6, 7].

EXPERIMENTAL

The set of foam concrete samples comprised of cement (Portland cement CEM I 42.5 R, Považská cementáreň, a.s., Ladce, Slovakia), water and technical

foam was prepared via pre-formed foaming. In all mixtures, constant water-cement ratio of 0.55 was maintained. The amount of cement and corresponding amount of water were lowered gradually until the destruction of the mixture was attained. Protein type (FN1) foaming agent was used to prepare the technical foam with bulk density of approximately 60 $kg \cdot m^{-3}$ by using the hand mixer. According our preliminary experiments, FN1 was diluted with water in the ratio of 1:28 to produce liquid foam with the above mentioned bulk density after 2 min of mixing.

On the basis of the results from our previous study [2], effectivity of FN1 was improved by its dilution to the half of original concentration and following microwave (2 min at 500 W) and ultrasonic treatment (6 min) before preparing the liquid foam. Sonication was performed in the Tesla UC 405 BJ-1 ultrasonic bath (25 kHz).

Cement and water mixing was carried out until a homogenous base mix without lumps of undispersed cement was achieved. Subsequently, full amount of the liquid foam was added to the cement paste gradually along with the continual stirring. After 5 min of homogenization, samples were poured into the plastic vessels with the volume of 0.5 l and left to hydrate and toughen in the air at laboratory temperature of 22 ± 1°C.

Selected mixtures were submitted to the water procedure as follows. 1 l of the mixture was poured into the same volume of the water, mixed up and left to settle for different times. After 1 min, 3 min or 10 min (series A) of sedimentation, the upper part of the mixture was homogenized in the separate vessel and then poured into the plastic vessels. Samples were left to cure in the same way as mentioned above. Water accumulated in the middle part of vessel and sediment were removed. Control experiments were carried out without subjecting of prepared mixture to the water procedure (series B).

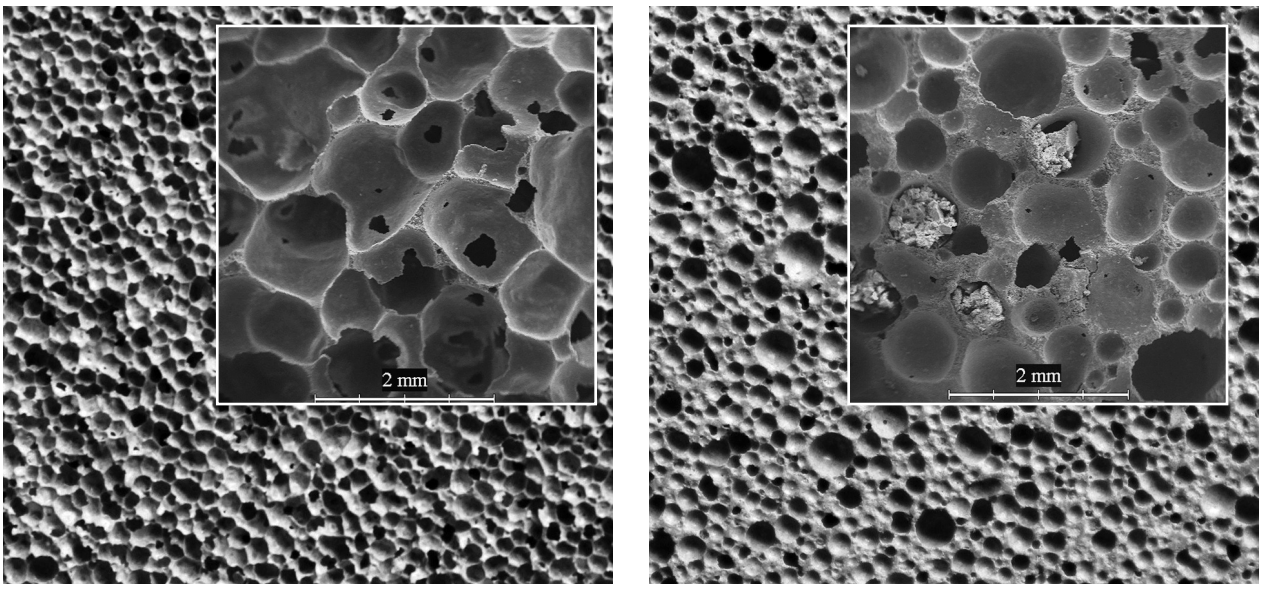
The development of temperature released as a result of hydration reactions evolution was recorded by means of calorimeter (OMEGA CN742). To achieve semi-adiabatic conditions, samples were placed in the plastic vessel insulated on all sides by 6 cm thick layer of polystyrene spheres. Temperature data were recorded every 10 min.

Wet (plastic) density of the samples was calculated from their weight and known volume of the vessels. After 21 days of drying and hardening in the air, the samples were dried at 100°C up to the constant weight and final bulk density was estimated.

The slices removed from the upper part of the samples approximately 0.5 cm from the border were observed by camera (CANNON EOS 650 D) and SEM (Tesla BS 300 with digitizing unit TESCAN). Samples were cleaned with compressed air to remove dust and lost particles. The mean pore size was determined from SEM micrographs by the linear intercept method [8]. Minimum of 200 pores was measured in order to obtain statistically robust set of data.

Pore size distribution was evaluated from SEM analysis by means of histogram and cumulative curve. Weibull curve was used to offset experiment data. Kolmogorov – Smirnov test (K–S test) of normality was carried out to verify justness of proposed theoretical function [9].

The presence of crystalline phases in the samples was evaluated after 21 days of curing by XRD analysis (STOE theta/theta diffractometer, Siemens Germany; CoKα radiation, λ = 0.179 nm, operating at 40 kV and 30 mA).



a) foam sample A_2 b) foam sample B

Figure 1. Microstructure of foam concrete prepared by water procedure (A2) and of foam concrete prepared by standard method (B). Middle sedimentation time (3 min) was used in this experiment.

RESULTS AND DISCUSSION

Microstructure

The use of water procedure led to the creation of more uniform and polyhedral microstructure of the foam concrete A_2. Average pore size is larger (Figure 1a; 690 μm) in comparison with the foam concrete B prepared by standard method (Figure 1b; 590 μm). Thickness of lamellas between polyhedral pores in foam concrete A_2 is very thin and reach sporadically the thickness of 2 μm (Figure 2). Particles with such and smaller size represent just about 1 % in the used Portland cement (Figure 3).

Pores in the foam concrete B which was prepared by standard method, thus without water procedure, retained spherical shape. The majority of pores reaches the size lower than 250 μm. The amount of pores with particular size descends with increasing pore size. In opposite, the highest frequency of pore size in the sample A_2 belongs to the interval between 400 μm and 600 μm. The use of water procedure resulted in essential reduction of pore size distribution (Figure 4a). The smallest and the largest pores disappeared from the samples of foam concretes. Whereas small pores (bubbles during the preparation) (below 200 μm) are pulled into the sediment, large pores (above 1100 μm) lose their stability due to very thin lamella thickness and terminate.

Measured experimental data displayed by means of histograms and cumulative curves were offset by mathematical Weibull function (Figure 4). Parameters of Weibull distribution function and results of Kolmogorov – Smirnov test are depicted in Table 1. Equally for both samples, the maximum value of absolute difference between theoretical and empirical distribution function did not overcome the value of $D_\alpha(n)$ for chosen 95 % significance level (α = 0.05). Accordingly, proposed Weibull distribution is statistically significant and could be used to describe measured set of data. In the case of sample B, Weibull curve reaches the maximum value

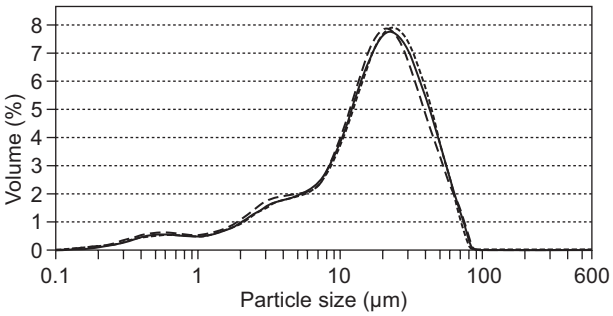
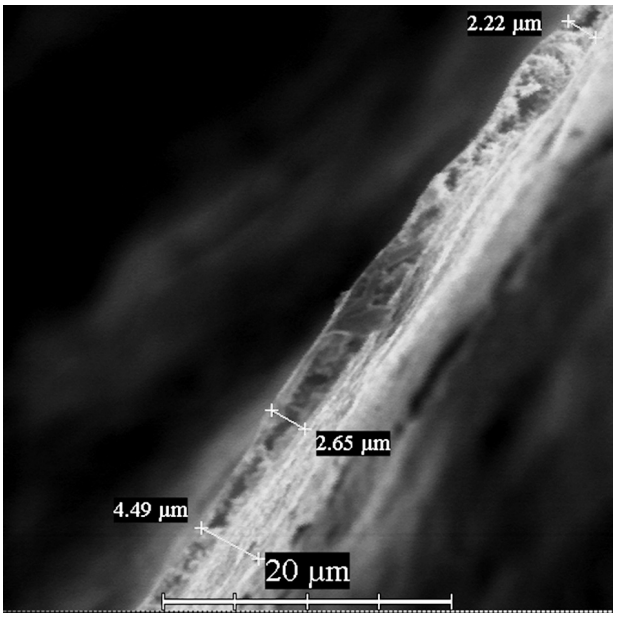
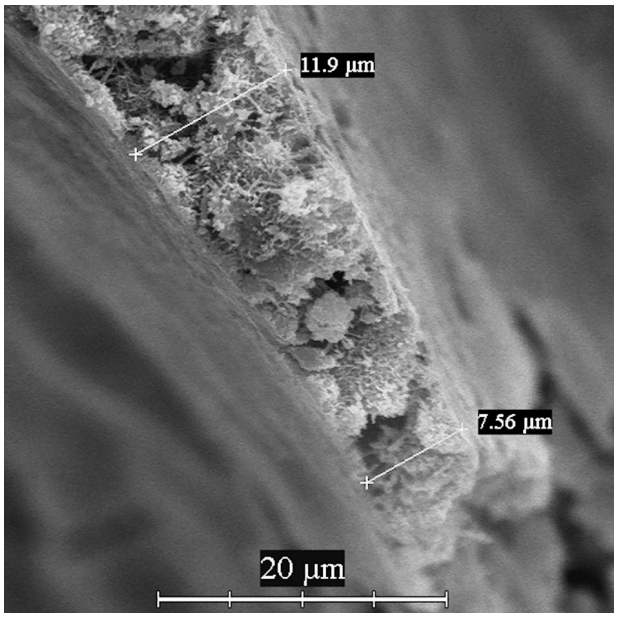


Figure 3. Particle size distribution of the used Portland cement CEM I 42.5 R.



a) foam sample A_2

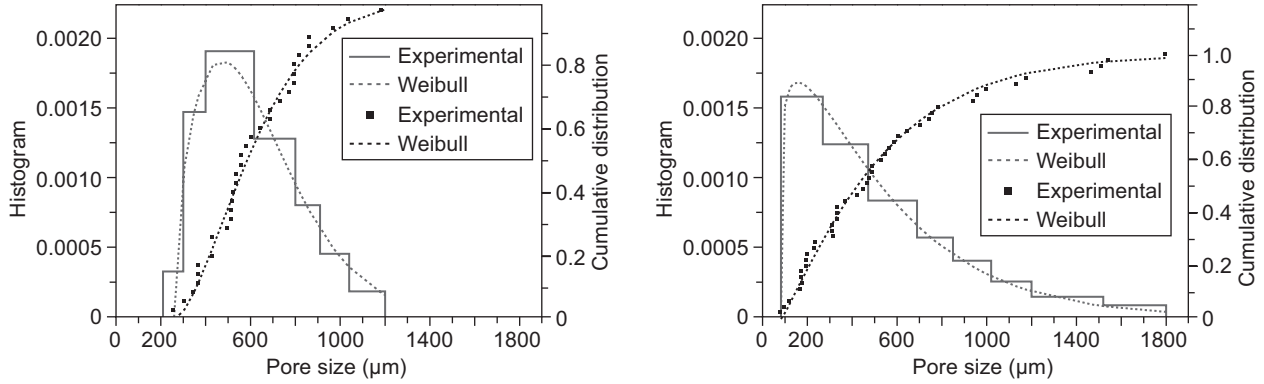


b) foam sample B

Figure 2. Detailed SEM of lamella in the foam sample A_2 and B respectively.

Table 1. Parameters of Weibull distribution functions and results of K–S test for samples A_2 and B.

Sample	*a*	*b*	*c*	*n*	max $\lvert F_n(x) - F(x)\rvert$	$D_\alpha(n)$; α = 0.05
A2	410.9049	1.5648	258.8810	200	0.0823	0.096
B	463	1.14	83.3280	200	0.0619	0.096



a) foam sample A_2 b) foam sample B

Figure 4. Pore size distribution of foam concrete prepared with the use of water procedure (A_2) and of foam concrete prepared by standard method (B).

for the pore size of 105 μm. Calculated maximum of function corresponding to the highest probability of pore occurrence moves to 407 μm for sample A_2.

As can be seen in Table 2, applying of water procedure resulted in significant reduction of bulk density. Cement particles are the main holders of the foam concrete weigh. Consequently they also attribute essentially to the bulk density of samples. Because cement particles which are not physically bond in lamellas are during the dilution with water pulled by gravity into the sediment, their amount in the final foam concretes decreases. This led to the observed drop of bulk density.

Table 2. Average pore size (APS) and final bulk density (BDF) of samples prepared from origin content of cement before (B) and after water procedure proceeding (A_1-A_3). APS and BDF of upper (U) and bottom (P) part of foam concretes underwent water procedure are estimated separately.

Sample		t_{sed} (min)	APS (μm)	BD_F (kg m^{-3})
A_1	U	1	660	140
	B		610	160
A_2	U	3	690	130
	B		650	150
A_3	U	10	1100	120
	B		1080	130
B	–	–	590	590

XRD results

The main crystalline phase in the samples of the foam concretes after 21 days of curing is portlandite (Figure 5). Except portlandite, calcite and unreacted dicalcium silicate were found in the samples prepared by water procedure (A_2). Calcite was not detected on the XRD pattern of sample prepared without the use of water procedure (B). Because calcite appears in the samples as a result of hydration products (portlandite and CSH) carbonation [10], its presence in sample A can be attributed to the higher rate of hydration reactions. This assumption is also supported by the calorimetric measurement results (Figure 5).

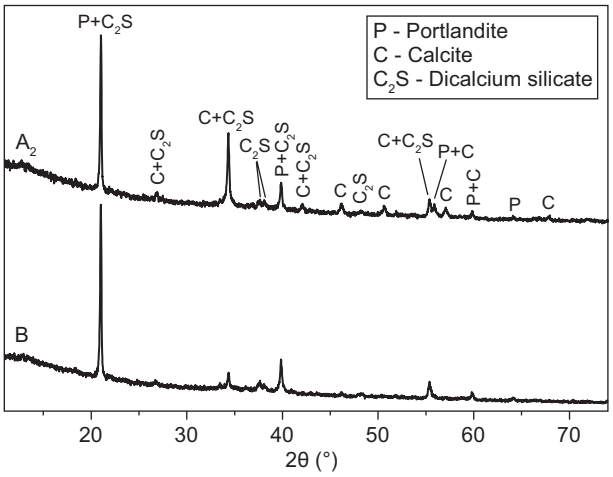


Figure 5. XRD pattern of sample prepared by water procedure (A_2) and of sample prepared by standard procedure (B) after 21 days of curing.

Effect of sedimentation time

Three sedimentation times (1 min, 3 min and 10 min) and their effect on microstructure and bulk density of samples were proved. In order to examine the effect of sedimentation time and connected destabilization mechanisms more in detail, samples were cut horizontally into two parts (designated as bottom and upper) and examined separately. As we can see from Table 2, prolongation of sedimentation time led to the increase of average pore size and decrease of final bulk density. Simultaneously, differences between upper and bottom parts of samples became more negligible. Higher time in

water resulted in higher sedimented amount of cement particles. Lamellas became thinner and thinner which resulted in the growth of larger pores at the expense of smaller ones – disproportionation started. Bottom parts of samples exhibited slightly lower average pore size when compared with particular upper parts. This can be explained by faster climbing up of larger pores towards the free surface of samples. Accordingly, parts lying lower contained smaller pores. In addition, cement particles descending down due to gravity did not have enough time to sediment at the bottom part of vessel when shorter times of water procedure were applied. This explains also smaller differences between APS and BD_F of parts in the case of longer sedimentation times.

The values of estimated final bulk densities correspond well and confirm the results mentioned above.

Calorimetric measurement

Calorimetric curves of the foam samples prepared by water procedure (A_1-A_3) and without that (B) are illustrated in Figure 6. Incorporation of water procedure into the preparation process led to the movement of the temperature curves to the earlier times. Maximum attained temperature is however higher in the case of sample prepared by standard procedure (40.3°C).

Although this higher temperature could indicate higher conversion of initial Portland cement minerals to the hydration products, most likely it is a result of larger amount of cement particles undergoing hydration. Abundance of water admixed into the cement slurry during water procedure caused the sedimentation of larger cement particles, which in turn eventuated in the decrease of bulk density of such prepared foam concrete (Table 2).

Higher rate of temperature increase observed on calorimetric curves of samples prepared by water procedure (A_1-A_3) can be assigned to the lower heat capacity. Rate of maximum temperature achievement

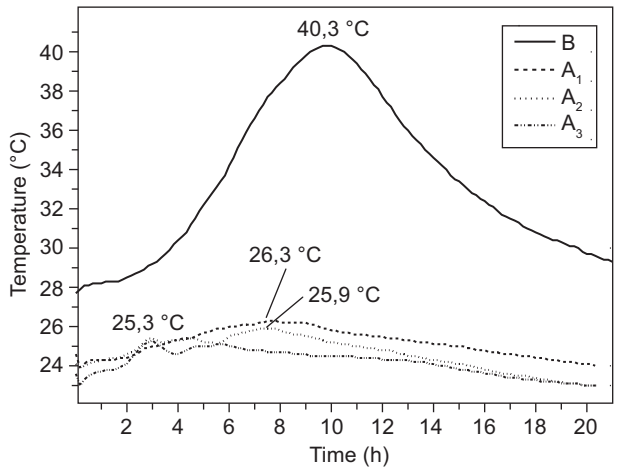


Figure 6. Time dependent temperature curves of the samples prepared by water (A_1-A_3) and by standard procedure (B).

increases with prolongation of sedimentation time. This also responds to the decreasing bulk density of samples (Table 3). The same effect of bulk density on temperature dependence of foam concretes was observed by Tarasov et al. [11]. Higher rates of hydration reactions in the case of samples A_1-A_3 is caused also by smaller size of cement particles undergoing hydration.

Temperature responding to the highest rate of hydration reactions descends with the prolongation of sedimentation time. Drop of maximum temperature is again caused by decreasing amount of respondent cement particles. If the amount of cement remained unchanged, lower bulk density of samples together with their higher porosity would lead to better conservation of heat inside the samples, which would on the contrary result in increase of temperature values [12].

On the time dependent temperature curve of samples sedimented for the time of 3 min and 10 min can be observed besides major also additional shoulder whose existence can be assigned to the different progress of hydration in the case of small cement particles.

Minimum cement content

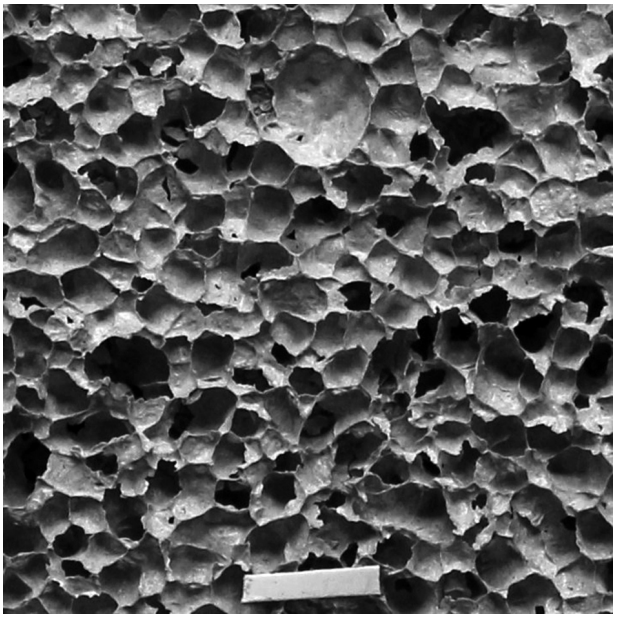
In these experiments, cement content was gradually lowered together with constant water-cement ratio keeping. Original state and concentration of FN1 (ordinary used in practice) was first used to clearly demonstrate the effect of foaming agent treatment under boundary conditions.

As was expected, average pore size increased with decreasing cement content. Every decreasing of cement amount for 20 % resulted in approximately 10 % increasing of average pore size (Table 3). Reduction of cement content to 30 % from its original amount was proved to be terminal and led to the collapse of the foams. It should be underlined that preparation procedure was optimized according to the preliminary experiments and despite lower amount of cement slurries, maximum possible homogenization of mixtures was achieved by slow and gradual additions of the liquid foams to the cement slurries. Degradation of the foams could be explained by insufficient amount of cement particles which were not able to stabilize bubbles in the liquid foams.

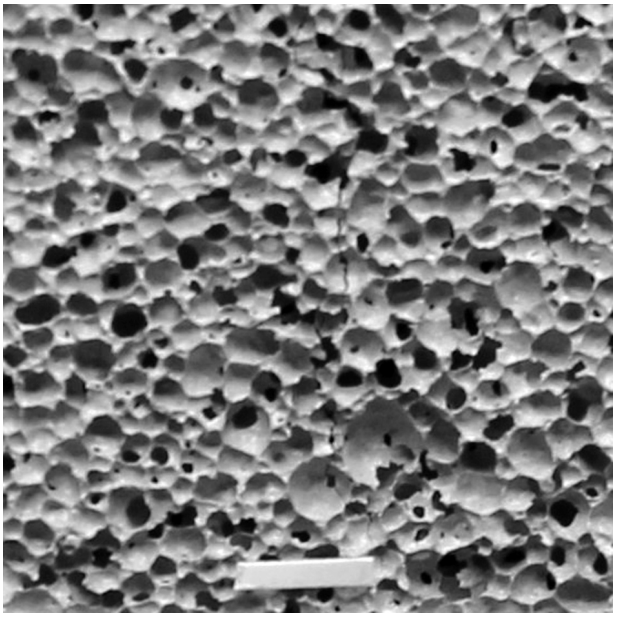
However when the protein based foaming agent was diluted to the half of its original concentration and microwave and ultrasonic treated before preparing the liquid foam, stability of the foams after cement incorporation was achieved (Figure 7b). In this way, insufficient amount of cement particles was compensated by higher activity (effectivity) of the foaming agent. Thus prepared foams were stable enough also after dilution with water during water procedure.

Applying of water procedure to the samples with 30 % of origin cement content led to the additional increase of average pore size (Figure 7a, Table 3). Final

bulk density reached the value of 95 kg·m^{-3}. As in the case of samples prepared with origin amount of cement, final bulk density decreased for more than 70 % when compared with the value of sample which was not submitted to the water procedure. Low bulk density of prepared samples is connected with relatively low strength. Even though, as well as water procedure also presented treatment of protein foaming agent point out to the great possibilities in the light foam concrete preparation. Our future work will be therefore focused on the improvement and optimization of strength of these lightweight foam concretes with the simultaneous maintenance of their low bulk density.



a) A_t30



b) B_t30

Figure 7. Microstructure of samples prepared without (B)/ with (A) applying of water procedure to the foams containing 30 % of origin cement content. Mixture sedimented in water for 3 min.

Table 3. The influence of gradually lowering cement content on the average pore size (APS) and final bulk density (BD_F) of samples prepared without applying of water procedure. Foamed samples containing 30 % of origin cement content and prepared with decreased concentration of microwave and ultrasonic treated FN1 are designated as A_t30 and B_t30. Mixture A_t30 sedimented in water for 3 min.

Sample	Treatment of FN1	APS (μm)	BD_F (kg m^{-3})
B100	untreated	770	690
B80		850	590
B60		940	480
B40		1040	310
B30		collapsed	
Bt30	treated	1500	390
At30		2300	95

CONCLUSION

Presented study dealt with possibilities of so called water procedure in the foam concrete preparation. Foamed samples were prepared by direct foaming method and with the use of protein foaming agent. It was revealed that modification of standard preparation procedure by dilution of samples with water represents promising way how to produce foam concretes with very low bulk density. In this way it is possible to prepare samples with more uniform and polyhedral microstructure. Much narrower pore size distribution in comparison with that of samples prepared by standard procedure is a result of crowding out and termination of the smallest and large bubbles from the mixtures during water procedure. Polyhedral microstructure of samples is developed due to draining of excessive water amount leading to the thinning of lamellas between bubbles. Required bulk density and microstructure of the foam concretes can be attained by assigning of optimal sedimentation time. Microwave and ultrasonic treatment of protein based foaming agent allowed us to reduce cement content up to 30 % of its original amount and still retain sufficient stability of prepared foams. Ultrasound and microwave heating increase the effectivity of protein foaming agent and thus compensate small amount of cement particles stabilizing bubbles. Applying of water procedure on the sample with lowered cement content led to the development of the foam concrete with bulk density of 95 kg·m^{-3}.

Although mechanical properties of such prepared samples are not convenient, there are still many open opportunities how to improve them to the appropriate

level. Enhancement of mechanical properties by means of various types of additives (e.g. polymers) constitutes therefore the aim of our following work.

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