The Influence of Some Surfactants on Porous Concrete Properties

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Expanded polystyrene is used as packing material in various industrial fields in the world. A large quantity of expanded polystyrene is consumed, and is disposed as a waste. On purpose to utilize packing tare waste of expanded polystyrene, composite material is created. The matrix in this composite material is porous concrete and insertion – crushed tare waste. The properties of composite matrix are analyzed comprehensively in this article. As it is known, porous concrete is one of types of lightweight concrete. One of ways to get porous concrete is the usage of surfactants in the formative mixtures. It has been widely used to decrease the density of concrete and to improve its thermal properties. The surfactant molecules help entrain air bubbles and stabilize them in the fresh cement paste. Researches with 6 different types of surfactants were made. The Ufapore TCO surfactant was chosen for the further research as the most suitable for production of composite material.

Keywords: porous concrete, surfactants, contact angle, surface tension.

INTRODUCTION

The use of lightweight concrete has been increasing especially in the construction of high rise buildings, off-shore structures and long span bridges due to the advantage of its low density, which results in a significant benefit in terms of load bearing elements of smaller cross section and a corresponding reduction in the size of the foundation [1]. There are two ways to reduce the density of concrete: using light porous fillers or forming air voids. These air voids are entrained in a fresh cement paste using surfactants [2]. Surfactants are substances, which have a tendency to concentrate at the surface or interface. They often carry a charge and thus they impart a charge to the surface that they attach to. To understand the role of surfactants play in this process, it is important to learn their chemical properties. The most common chemical classification of surfactants is based on the nature of the hydrophilic group, i. e., anionic (the surface-active portion of the molecule exhibits a negative charged), cationic (the surface-active portion bears positive charge), zwitterionic (both, positive and negative charges are presented in the surface-active portion), nonionic (the surface-active portion bears no apparent ionic charge) [3]. The first three classes create the group of ionic surfactants. As Shenfeld [4] prescribes, hydrophilic and hydrophobic nature of surfactant molecules determines their solutions behaviour. Temperature also affects the solubility of surfactants. The solubility of ionic surfactants increases rising the temperature while nonionic – decreases [5].

Micelle formation is an important parameter due to a number of important interfacial phenomena, such as detergency and solubilization, depend on the existence of micelles in surfactant solution [3]. If the concentration of surfactants in a volume of the system does not exceed the concentration in the interfacial surface, molecules and ions are the monodispersic conformation. Increasing the concentration of surfactants in a volume of the system, it starts to exceed the concentration in the interfacial surface and than micelles are formed. The concentration of surfactant solution at which remarkable changes of its properties begin because of micelle formation is called the critical micelle concentration (CMC) [6]. Then all the coaligative properties of the solution fluctuate. The ionic surfactants modulate into micelles when moll concentration is ten times higher than nonionic surfactants [5]. Rosen [7] fixed that the value appearing first to decrease with the temperature to some minimum and then to increase with further increase in temperature, so the effect of temperature on the CMC in aqueous solutions of surfactants is very complex.

It is known that formed air bubbles in fresh concrete are unstable and have a limited lifetime. The interfaces between the dispersed air and the surrounding matrix contain free surface energy, and the thermodynamic tendency is to reduce the interfacial surface areas [8]. Diffusion of air from a bubble, bubble coalescence due to capillary flow, and rapid hydrodynamic drainage of liquid from the bubbles show that pure liquid cannot form stable air bubbles [9]. Girniene et al. [10] investigated the influence of different surfactants and stabilizers on the foam stability in porous concrete production technology and fixed that this stability is the main factor affecting the selection of surfactants. Most of modern surfactants have anionic nature, because the stability of air voids is generated in assistance with them [11]. The stability of air voids is questionable when they are formed using the cationic and nonionic surfactants [8]. Fagerlund [12] described three mechanisms of air-void instability in the concrete. Mielenz et al. [13] proposed four origins of air in the concrete, which include air contained in the system and air entrapped during the mixing. Bruere [14] specified factors affecting the air entrainment in cement and silica pastes, Powers [15] described how air is entrained into concrete mixture during the mixing, Diamond [16] analyzed how mixing time affecting microstructure in concrete and Monteiro et al. [17] examined air void morphology in the fresh cement pastes. Authors [18] analyzed adsorptive behavior of the

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surfactants on a surface of Portland cement. It is widely known that the pore structure of concrete strongly influences its physical properties [19, 20].

The aim of this work is to investigate the properties of aqueous solutions of some surfactants and the influence of different surfactant type, concentration and mixing time on the density of fresh cement paste and hardened specimens. Depending on research results to choose the most suitable surfactant type from several ones, its optimal content and mixing time.

EXPERIMENTAL

Portland cement of mark CEM I 42,5R from the company JSC "Akmenės cementas", which met requirements of the standard [21], was used as a binding material. Portland cement setting time is 140 min and final setting time – 190 min [22]. The specific surface area according to Blaine was 420 m^2/kg. The chemical and mineral compositions of Portland cement were determined in accordance with the methods [23] and [24], respectively, and are presented in Table 1.

For the determination of surfactant solution properties, aqueous solutions from distilled water and following surfactants (air entraining agents are also called surfactants in this article) were studied: (a) Ufapore CC 85; (b) Ufapore TP 707; (c) Upafore CC; (d) Ufapore TCO; (e) PB-2000 and (f) Sulfonol-bone glue. These surfactants were used in contents: 0.025, 0.050, 0.075, and 0.100 %. Key properties of surfactants are presented in Table 2.

The measure of surface tension was made with Rebinder apparatus. The distilled water was poured into the test – tube and the capillar of pipe was contacted to the surface. Dripping the distilled water from aspirator the maximal difference between liquid heights was fixed in the manometer offsets. Then the mostly attenuated solution of surfactant is poured not varying the speed of water dripping from aspirator and the difference between heights is measured in the manometer offsets again. The measurements are made with all rising contents solutions of surfactants. The measurements are made three times, the average of data is used in the calculations. The surface tension was calculated in following way:

$$\sigma_X = \frac{\sigma_0 \cdot h_X}{h_0}, \tag{1}$$

where σ_0 is the surface tension of distilled water, σ_X is the surface tension of surfactant solution, h_0 is the difference between heights in a manometer offsets of distilled water, h_X is the difference between heights in a manometer offsets of surfactant solution.

It is impossible to determine the contact angle of a drop of surfactant solution onto the surface of crushed expanded polystyrene waste. Accordingly these angles were measured onto the surface of metallic plate coated with the paraffin wax. The position of a drop was fixed with the VARIMEX projector. The variation of contact angle was measured depending on the content of surfactant solution.

After determination of surface tension and contact angle it is possible to fix the wetting of surfactant solution. Wetting is also characterized in terms of a "work of adhesion" denoted by W_{Ad}, and calculated in the following way:

$$W_{Ad} = \sigma_{lv}(1 + \cos\theta), \tag{2}$$

where W_{Ad} is the work of adhesion, σ_{lv} is the surface tension of the liquid, θ is the contact angle at the solid-liquid-vapor contact region.

For the formation of the fresh cement pastes the same surfactants, mentioned above, were used (W/C ratio = 0.3).

These surfactants were used in contents: 0.01, 0.03, 0.05, 0.07 and 0.09 % (calculating from Portland cement mass).

For materials mixing, the round plastic container of 20 liters and the vertical mixer MXP1602E was used. During the whole mixing, the speed of a mixer was 225 r.p.m.

Table 1. Chemical and mineral compositions of Portland cement

Chemical composition	SiO_2		Al_2O_3		Fe_2O_3		CaO		$K_2O + Na_2O$	SO_3	Others
In %	20.76		6.12		3.37		63.50		1.03	0.80	0.30
Mineral composition		C_3S		C_2S		C_3A		C_4AF			
In %		58.54		15.29		10.40		10.17			

Table 2. A summary of the major physical properties of the surfactants used in this study

	Ufapore CC 85	Ufapore TP 707	Ufapore CC	Ufapore TCO	PB-2000	Sulfonol-bone glue
Chemical description	Air entraining agent	Anionic surfactant	Mixture of anionic and non-ionic surfactants	Air entraining agent	Foamer	Anionic surfactant
pH	7.8	10.7	8.8	8.0	7.0 – 10.0	8.0
Molecular mass, g/mol	–	382	–	–	–	290
Appearance	White colored	Pale straw paste	Clear mobile liquid	White colored	Brown colored	Yellow colored
Active content, %	85.3	27.2	30.1	92.0 – 96.0	–	75.0

The density of the fresh cement paste was fixed after every 2 mixing minutes. The round metallic can of 0.5 liter was used for that purpose. Density of fresh cement paste was fixed by weighting empty and filled with fresh cement paste metallic can. The density of the fresh cement paste was fixed till 34 mixing minute.

The density of hardened specimens of the porous concrete was fixed after 4, 8, 14 and 24 mixing minutes. The prepared cement paste was poured into molds (size (10×10×10) mm) and slightly compacted to have the paste evenly distributed. The following day the molded specimens of porous concrete with different densities were taken out of molds, covered by polyethylene film and kept for 27 days at temperature of 20 °C. Afterwards, the specimens were conditioned in the ventilated oven until constant mass was achieved. After that specimens were measured and the density of hardened specimens was fixed.

The pore structure of the hardened specimens was determined by an optical microscope, connected to a computer, which can enlarge the image up to 100 times.

RESULTS AND DISCUSSIONS

Low surface tension of the liquid phase helps to entrain air bubbles in fresh cement paste during the mixing. In many liquid – solid systems, wettability is also improved lowering the surface tension of the liquid phase. Research results showed that all surfactant solutions in all contents reduced the surface tension comparing with pure distilled water (0.073 N/m). Ufapore CC 85 surfactant solution has the lowest values of surface tension (from 0.051 N/m to 0.035 N/m) in all contents. PB-2000 surfactant solution has the highest value of surface tension (0.051 N/m) in 0.025 % content, and Ufapore CC has the highest values (from 0.048 N/m to 0.036 N/m) in contents from 0.050 % to 0.100 %.

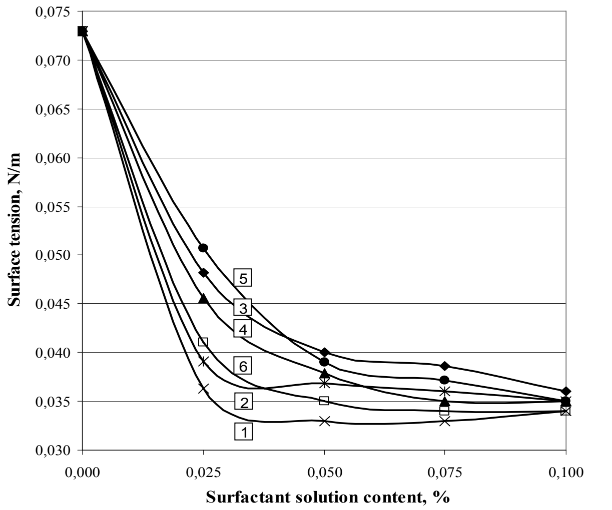

Fig. 1. The dependence of surfactant solution surface tension on its content and type: 1 – Ufapore CC 85; 2 – Ufapore TP 707; 3 – Ufapore CC; 4 – Ufapore TCO; 5 – PB-2000; 6 – Sulfonol-bone glue

The angle of contact θ is measured through the liquid at the solid-liquid-vapor contact region after the liquid has attained an equilibrium configuration on the solid. Low values of θ will be obtained if the liquid surface tension is low, the surface energy of solid is high, and the liquid-solid interfacial tension is low [25]. The solid is wet by the liquid, if $\theta < 90°$ and if $\theta > 90°$, the solid is not wet by the liquid. Research results showed that Ufapore CC 85 surfactant solution has the lowest θ value (41º) in content 0.025 %, Ufapore TCO (32º and 33º) in contents 0.050 % and 0.075 %, and PB-2000 (36º) in content 0.100 %. The highest θ value (62º) was fixed with PB-2000 surfactant solution in content 0.025 %, and Ufapore TP 707 (from 61º to 59°) in contents from 0.050 % to 0.100 %.

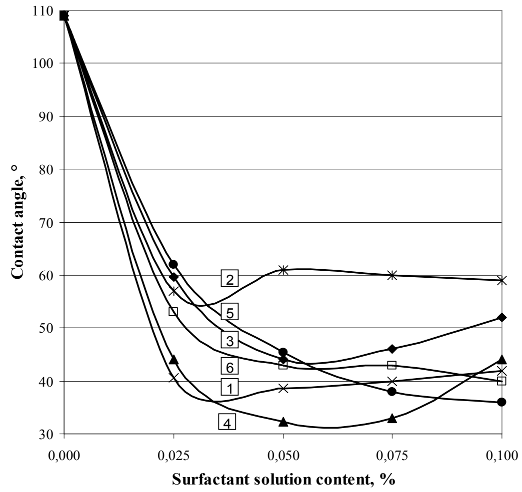

Fig. 2. The dependence of surfactant solution contact angle on its content and type: 1 – Ufapore CC 85; 2 – Ufapore TP 707; 3 – Ufapore CC; 4 – Ufapore TCO; 5 – PB-2000; 6 – Sulfonol-bone glue

A high value of W_{Ad} indicates good wetting, and low value – poor wetting. Good wetting means that the strong adhesion between the liquid and the solid will develop. Research results (Fig. 3) showed that Ufapore TCO surfactant solution has the highest work of adhesion values (from 0.078 N/m to 0.070 N/m) in contents (from 0.025 % to 0.050 %) and PB-2000 the highest values (from 0.066 N/m to 0.063 N/m) in contents (from 0.075 % to 0.100 %). The Ufapore TP 707 surfactant solution has the lowest values (from 0.060 N/m to 0.053 N/m) in all contents.

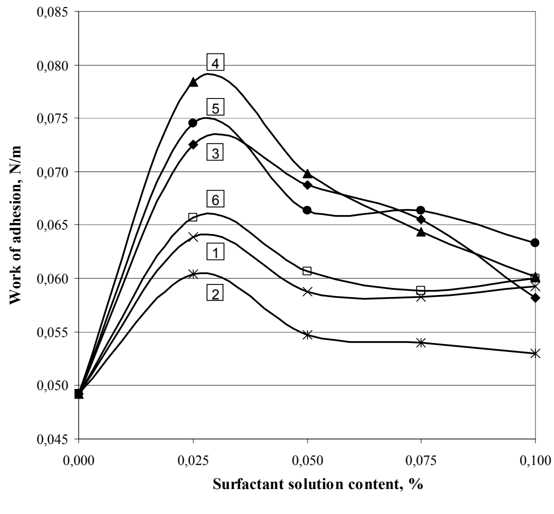

Fig. 3. The dependence of work of adhesion on surfactant solution content and type: 1 – Ufapore CC 85; 2 – Ufapore TP 707; 3 – Ufapore CC; 4 – Ufapore TCO; 5 – PB-2000; 6 – Sulfonol-bone glue

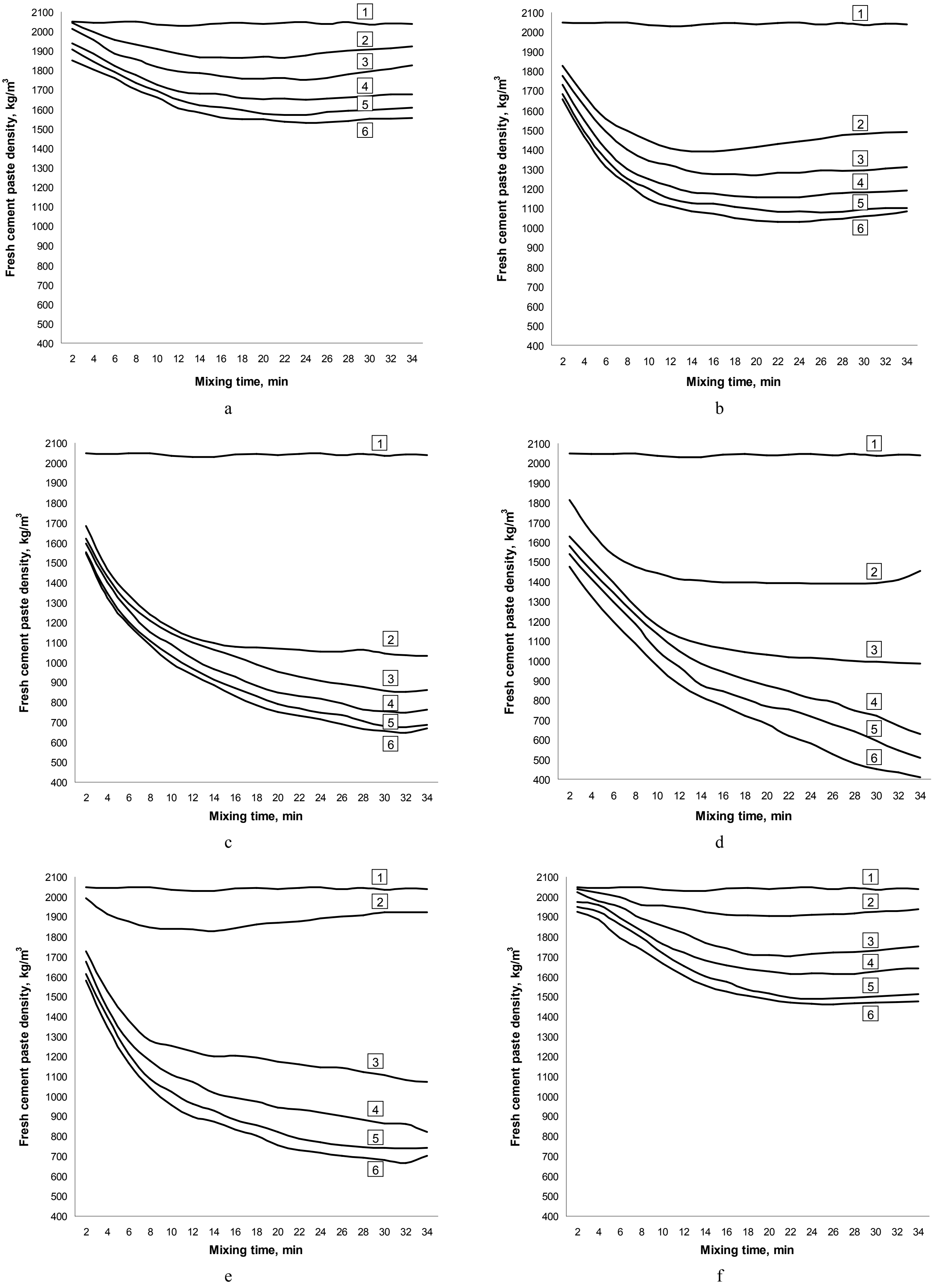

Fig. 4. The changes of fresh cement paste densities depending on surfactant type, content and mixing time: a – Ufapore CC 85, b – Ufapore TP 707, c – Ufapore CC, d – Ufapore TCO, e – PB-2000, f – Sulfonol-bone glue. 1 – test, 2 – 0.01 %, 3 – 0.03 %, 4 – 0.05 %, 5 – 0.07 %, 6 – 0.09 %

After the analysis of surfactant solution properties the density of the fresh cement pastes was fixed. There is no sense in mixing the fresh cement paste longer than for 10 minutes in the technological processes of this composite material type, so the effectiveness of surfactants must be estimated depending on this factor. It was established that the most effective are Ufapore CC and Ufapore TCO surfactants in all contents (Fig. 4, c and d). Although primary decrease of the density of fresh cement paste with Ufapore CC surfactant is more significant, the density of cement paste with Ufapore TCO surfactant decreases more rapidly then the content of surfactant is enlarged. The density values of the fresh cement paste with mentioned surfactants vary from 1684 kg/m^3 to 996 kg/m^3 (Ufapore CC), and from 1812 kg/m^3 to 973 kg/m^3 (Ufapore TCO) when mixing time was till 10 minutes. It was found that the less effective are Ufapore CC 85 and Sulfonol-bone glue surfactants (Fig. 4, a and f) in all contents and through all mixing ranges. The density values of the fresh cement paste with mentioned surfactants through all mixing ranges vary from 2044 kg/m^3 to 1554 kg/m^3 (Ufapore CC 85) and from 2040 kg/m^3 to 1477 kg/m^3 (Sulfonol-bone glue).

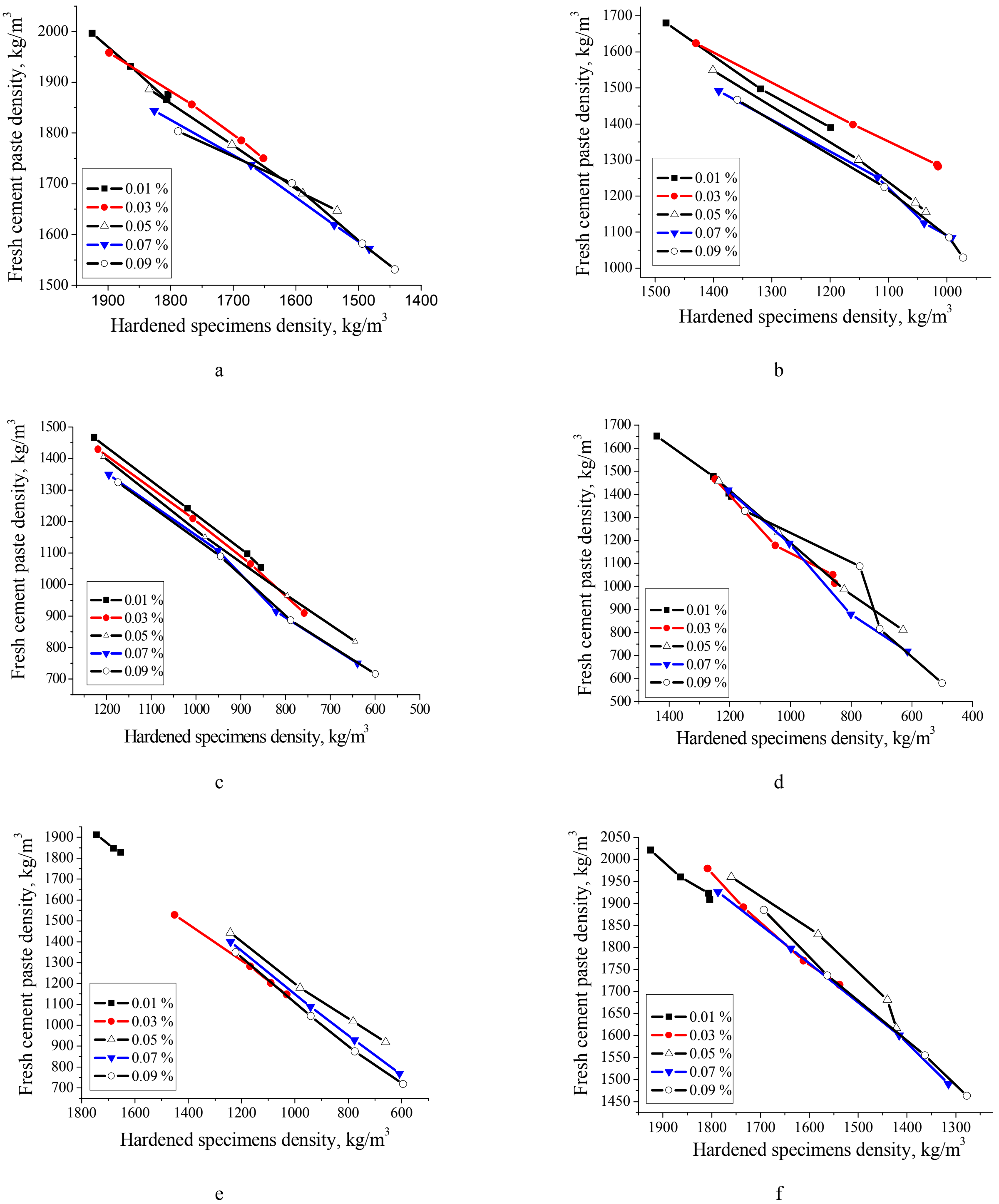

Fig. 5. The dependence of hardened specimens density on the fresh cement paste densities: a – Ufapore CC 85, b – Ufapore TP 707, c – Ufapore CC, d – Ufapore TCO, e – PB-2000, f – Sulfonol-bone glue

The dependences of hardened specimen densities on fresh cement paste densities showed that lower value of fresh cement paste density will cause the decrement of hardened specimen density values in all contents and mixing ranges. It was fixed that the less effective surfactant is Ufapore CC 85 (Fig. 5, a). The density values of hardened specimens of mentioned surfactant vary from 1925 kg/m^3 (0.01 %) to 1531 kg/m^3 (0.09 %). The most effective surfactant in contents (from 0.01 % to 0.05 %) is Ufapore CC. Its values vary from 1228 kg/m^3 to 644 kg/m^3. Moreover, surfactants PB-2000 and Ufapore TCO had the lowest density values of hardened specimens (from 942 kg/m^3 to 608 kg/m^3 and from 1150 kg/m^3 to 500 kg/m^3) in contents (from 0.07 % to 0.09 %) accordingly. It is important to mention, that there is no big difference between the values of hardened specimens of both Ufapore CC and TCO surfactants. Both of them are more effective even in low contents comparing with other ones.

The pore structure analysis of hardened specimens showed that after 8 mixing minutes Ufapore CC surfactant in content 0.03 % formed pores of very large diameter, comparing with other surfactants in the same content (Fig. 6, c). This determination explains why the density of fresh cement paste and hardened specimens, formed with this surfactant, has the lowest values. The thin partitions between pores were formed and this leaded to the coalition of adjacent air bubbles. Analogous phenomenon was fixed in Ufapore TP 707 and PB-2000 surfactants (Fig. 6, b and e). In contrast with surfactants mentioned above, Ufapore CC 85 and Sulfonol-bone glue formed pores of small diameter (Fig. 6, a and f), as a result the density of fresh cement pastes and hardened specimens had the highest values. However, Ufapore TCO formed pores of larger diameter comparing with Ufapore CC 85 and Sulfonol-bone glue surfactants. It determined lower density values of fresh cement pastes and hardened specimens. Thicker

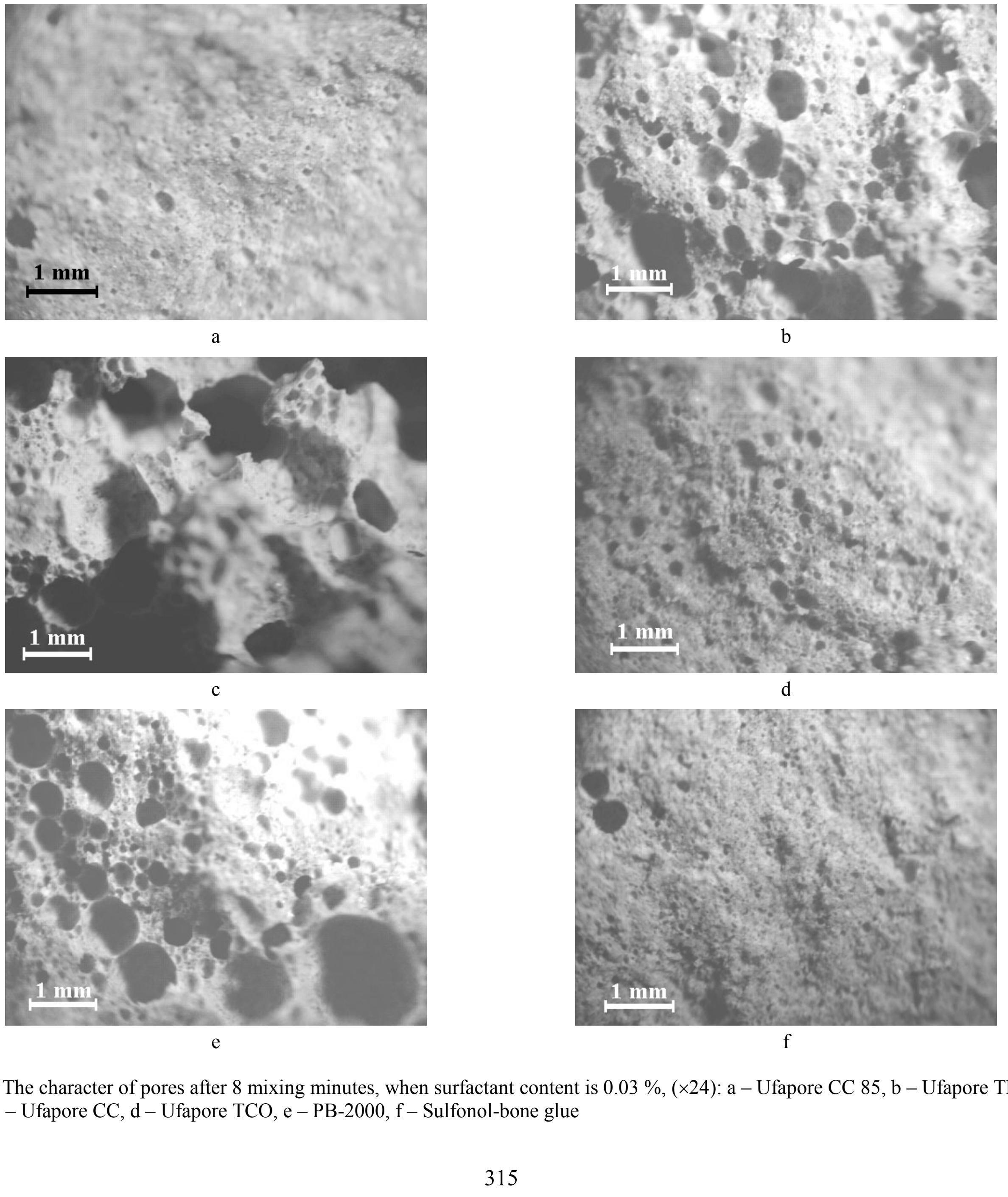

Fig. 6. The character of pores after 8 mixing minutes, when surfactant content is 0.03 %, (×24): a – Ufapore CC 85, b – Ufapore TP 707, c – Ufapore CC, d – Ufapore TCO, e – PB-2000, f – Sulfonol-bone glue

partitions between pores helped to avoid their coalition, so formed air bubbles were more stable and the existence of large diameter pores (which are not desirable) was not fixed (Fig. 6, d).

CONCLUSIONS

1. It was established that all types of surfactants in all contents reduced surface tension and contact angle of distilled water. It means that all surfactants improve the wetting ability of crushed expanded polystyrene waste with fresh cement paste.

2. The measurements of fresh cement paste and hardened specimens densities showed that the most effective surfactants are Ufapore CC and Ufapore TCO. The optimal content of them should not exceed 0.03 %. The usage of these surfactants in higher contents is not economically effective.

3. Research results showed that mixing time with mixer MXP1602E should not exceed 10 minutes. Almost all types of surfactants reduce most part of porous concrete primary densities till that time. Longer mixing time is useless economically and technologically.

4. Although surfactant Ufapore CC reduces the value of porous concrete density a little bit more effective than surfactant Ufapore TCO, but analysis of the structure showed that pores of large diameter and connected between each other are formed when the mentioned surfactant is used. This type of voids can influence the properties of all composite material negatively in the matrix of composite. This does not work with the second surfactant. So, the surfactant Ufapore TCO will be used to reduce the density of matrix in the further stages of composite creation.

5. It is estimated experimentally that Ufapore TCO aqueous solution has the best wetting in contents (from 0.025 % to 0.050 %) comparing with other surfactants. For further research, surfactant Ufapore TCO will be also used as a material which improves coating of crushed expanded polystyrene waste with cement matrix.

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