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THE STUDY OF AUTOCLAVED CELLULOSE FIBER-REINFORCED CEMENT COMPOSITES

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ABSTRACT

The effects of individual or combined addition of sodium water glass (SWG), calcite and $CaCl_2$ into the starting material, consisting of 92 wt.% of Portland cement with sand and 8 wt.% of cellulose fibers, were studied after autoclaving. Bending strength, bending toughness and module of elasticity were determined. The optimal additions were either 26 wt.% of SWG and 10 wt.% of calcite (sample No. 4) or 5 wt.% of $CaCl_2$ (sample No. 2). Autoclaved products were also investigated by X-ray diffraction (XRD), mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM). All results were compared to the product obtained without additions.

Introduction

Although some countries have already mastered the production of autoclaved cellulose fiber-reinforced cement composites (ACFRCC) (1) there is still an active research going on due to low price of cellulose fibers (2). The investigators direct their research mostly into the modifications of starting materials by various additives in order to be able to carry out the production process according to the already established techniques for the manufacture of asbestos-cement products, and with less emphasis on final properties of ACFRCC products (3).

A comprehensive study (4) reported on the investigation of autoclaved ACFRCC products that were initially made of 92 wt.% of Portland cement with sand (50:50) and 8 wt.% of cellulose fibers (Pinus radiata). The research was carried out after a 10-hour autoclave treatment at 180°C under saturated steam conditions and also after several years of aging. It was ascertained that several factors contributed to an increase in bending strength of ACFRCC after aging but the emphasis was also given to the decrease of larger, slit-like pores while total porosity remained virtually unchanged. However, the correlation between total porosity and bending strength was not found (5). The same paper reported that larger pores controlled the strength, which was independent of volume fraction of pores but depended on pore size distribution. Other work (6) put emphasis on the effect of individual pore fractions and to the dimension and shape of larger pores. The increase of compressive strength with an increase of amount of 1.1 nm tobermorite in products obtained by 2 to 64 hour autoclaving at 180°C of lime, cement, SiO_2 and Al_2O_3 was also indicated (7). The compressive

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Abbreviations: C=CaO, S=SiO_2, H=H_2O

strength of autoclaved products obtained under similar conditions, but made from white Portland cement with the addition of either silica fume or silica sand, was found to be linearly related to the sum of Q_1-, Q_2-, and Q_3-type of silicate anions (determined by ^{29}Si CP-MAS NMR spectroscopy). The addition of silica fume decreased the strength of the products due to the presence of silicate anions as dimeric forms (8).

The relationship between pore diameter and the distribution of amorphous C-S-H phase in cement stone (9) was studied by small angle neutron scattering (SANS). Pores with diameter larger than 60 nm were found in samples which had C-S-H phase distributed on the surface of clinker particles; pores with diameter between 10 and 60 nm were found for samples that had C-S-H aggregates distributed among clinker particles, whereas pores of 5 nm diameter were found to be present within C-S-H gel.

Our work reports on the modification of starting mixture (92 wt.% of Portland cement with sand (60:40) and 8 wt.% of cellulose fibers) by the addition of SWG and calcite or $CaCl_2$. We report on qualitative course of hydrothermal reactions, on porosity and on pore size, shape and distribution. Also given are data on bending strength, bending toughness and module of elasticity.

Experimental

Portland cement (Building materials industry Salonit Anhovo, Anhovo, Slovenia) of the following composition was used: CaO, 54.3 wt.%; SiO_2, 20.1 wt.%; Al_2O_3, 5.9 wt.%; Fe_2O_3, 2.5 wt.%; MgO, 2.3 wt.%; SO_3, 2.0 wt.%; MnO, 0.2 wt.%; loss on ignition, 2.7 wt.%. Specific surface area of portland cement with sand (60:40) was 4800 cm^2/g (Blaine).

Quartz sand had the following composition: SiO_2, 96.2 wt.%; Al_2O_3, 0.7 wt.; Fe_2O_3, 0.7 wt.%; loss on ignition, 0.4 wt.%.

Calcite (Building materials industry Salonit Anhovo, Anhovo, Slovenia) with the following composition was used: CaO, 54.2 wt.%; SiO_2, 1.6 wt.%; P_2O_5, 1.0 wt.%; MgO, 0.3 wt.%; loss on ignition, 42.7 wt.%. Its specific surface area was 4 m^2/g (BET N_2 method).

Sodium water glass (Alumina and aluminum factory Kidricevo, Kidricevo, Slovenia) with 33 wt.% SiO_2 and 11 wt.% Na_2O, SiO_2/Na_2O = 3.0, was used.

$CaCl_2$ was of reagent quality.

Cellulose fibers 'Orion' (Factory Poels, Poels, Austria) were sulphate-cellulose fibers, ground to 30°SR (Schaper Riegler) with the average fiber length of 1.9 mm. Fibers comprised 95 wt.% of pine wood fibers and 5 wt.% of birch wood fibers.

Samples with the diameter of 58 mm and height of 6-10 mm were prepared from starting material (92 wt.% of Portland cement with sand (60:40) and 8 wt.% of cellulose fibers) with the following additions: calcite (5, 10, and 15 wt.%), $CaCl_2$ (0.2, 0.4, 1.0, 1.3, 2.0, and 5.0 wt.%) and SWG (6.5, 13.0 and 26.0 wt.%). Water/solids ratio was always 4.0. The same experimental procedure (preparation, filtering and pressing) was used throughout. After autoclaving for 6 hours at 180°C under saturated steam conditions, the products were dried for 6 hours at 105°C.

Bending strength was measured by the three-point method (10) on an Instron 1195 instrument with the speed of 1 mm/min. The module of elasticity was calculated at maximum bending strength; bending toughness was calculated as integral area under the curve bending strength - deflection.

Qualitative course of hydrothermal reactions in products with optimal properties, samples No. 2 and 4, as well as of reference product, sample No. 1, was evaluated by XRD, SEM, MIP (pressure up to 207 MPa and with the contact angle of 145 degrees), and weight loss measurement up to 900°C.

Results and Discussion

Figures 1, 2a and 2b show bending strength, module of elasticity and bending toughness for product with unmodified starting mixture as well as for the ones containing the additions of SWG, calcite and $CaCl_2$. Maximum increase in both bending strength and bending toughness and the decrease of the module of elasticity was obtained with the addition of either 26 wt.% of SWG and 10 wt.% of calcite (sample No. 4) or 5 wt.% of $CaCl_2$ (sample No. 2) if compared to reference product obtained by autoclaving the starting mixture without any additives. These differences can also be seen on figure 2c as characteristic load - deflection curves.

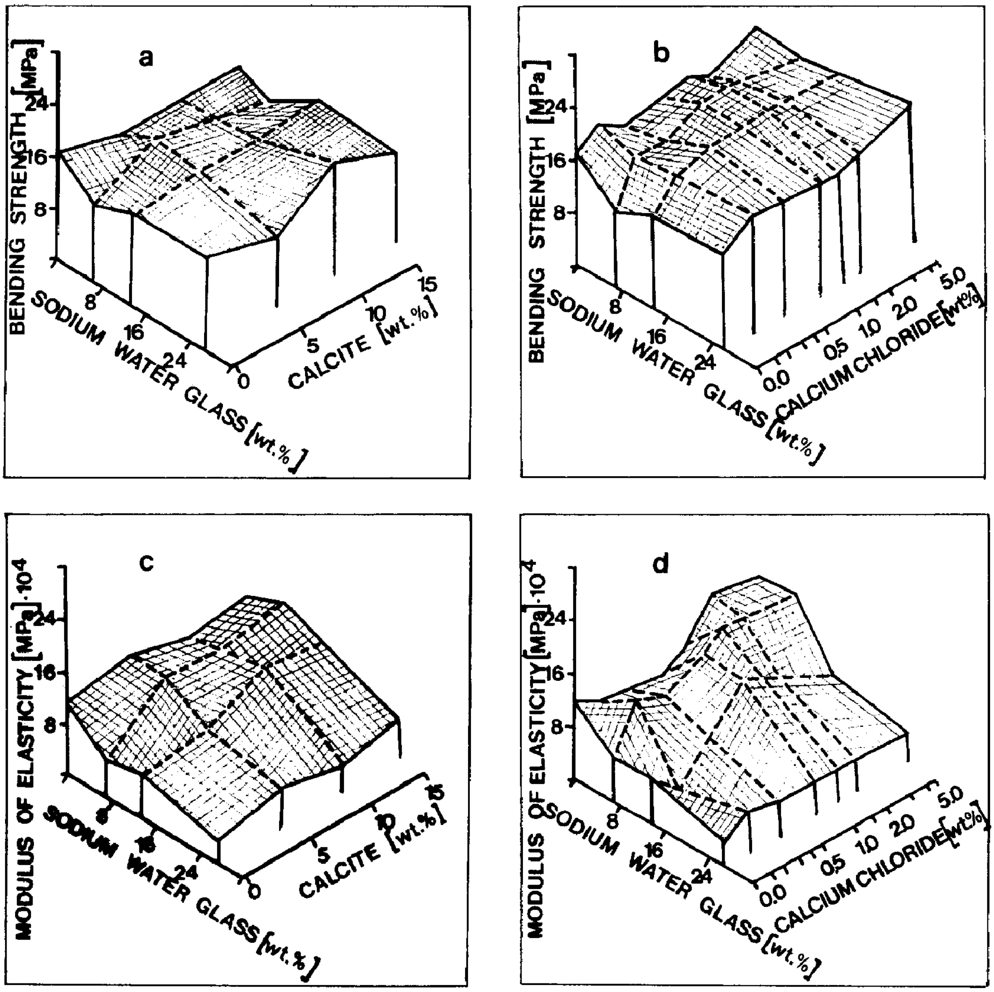

Fig. 1

Bending strength versus added SWG and calcite (a) or $CaCl_2$ (b) and modulus of elasticity versus added SWG and calcite (c) or $CaCl_2$ (d)

Bending strength and bending toughness of sample No. 4, if compared to the result for reference sample, increased by 23 % (from 16.3 to 20.0 MPa) and by 81 % (from 1.6 to 2.9 kJ/m^3), respectively. The module of elasticity decreased by 58 %

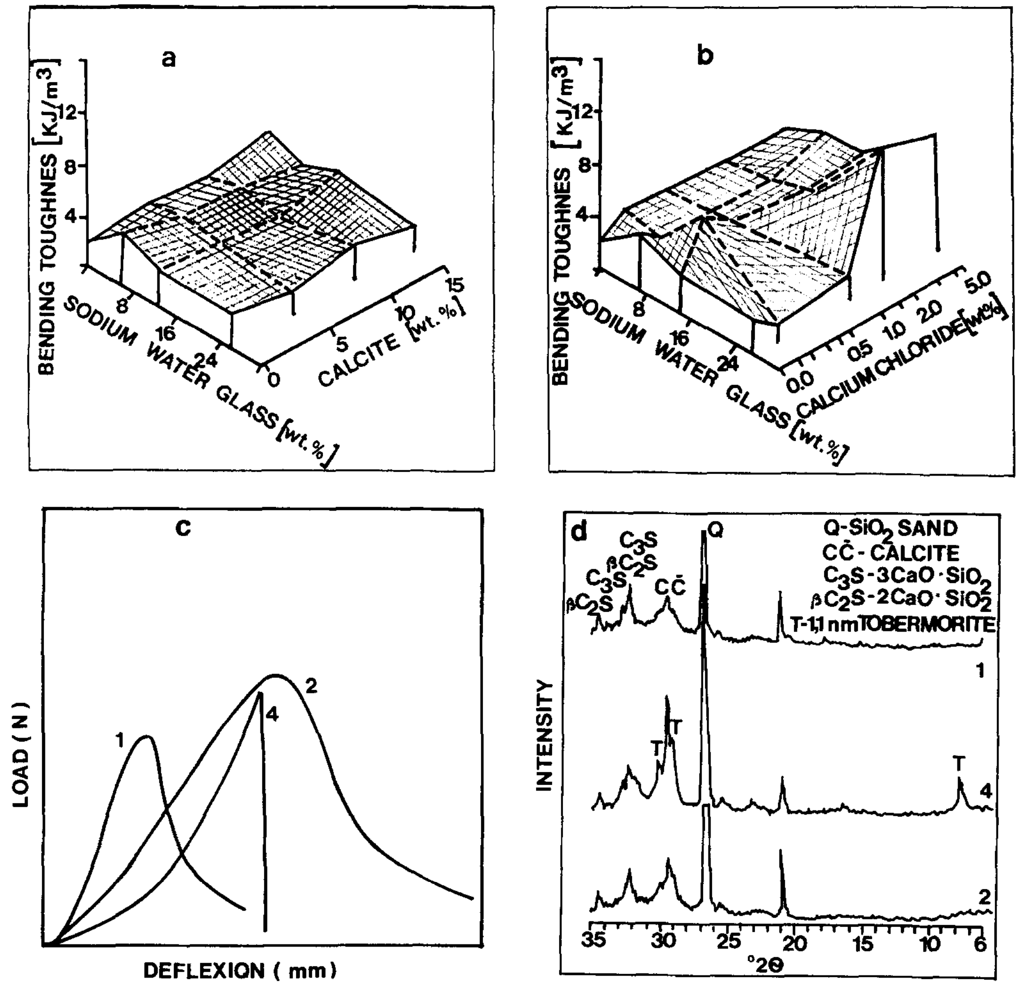

Fig. 2

Bending toughness versus the addition of SWG and calcite (a) or $CaCl_2$ (b) and characteristic load - deflection (c) curve and XRD patterns (d)

(from $11.2.10^{-4}$ to $4.7.10^{-4}$ MPa). The corresponding values for sample No.2 were: an increase of bending strength and bending toughness by 35 % (from 16.3 to 22.0 MPa) and 456 % (from 1.6 to 8.9 kJ/m^3), respectively. The module of elasticity decreased by 64 % (from $11.2.10^{-4}$ to $4.0.10^{-4}$ MPa). The same increase in bending toughness and a somewhat smaller increase in bending strength was achieved with the addition of 26 wt.% of SWG and 2 wt.% of $CaCl_2$.

The course of hydrothermal reactions followed by XRD and weight loss measurements of the above samples is given in figures 2d, 3a and 3b. Sample No. 4 shows, if compared to reference sample No.1, lower intensities of XRD reflections corresponding to SiO_2, C_3S, and C_2S and higher intensity of basal (002) reflection of 1.13 nm tobermorite. Greater weight loss of sample No. 4 at 300°C is related to the amount of 1.13 nm tobermorite (11), whereas the weight loss between 600°C and 800°C is due to the decomposition of calcite (figures 3a and 3b).

XRD spectrum of sample No. 2 shows lower intensities of tri- and dicalcium silicate and higher intensity of quartz in comparison with reference sample No. 1. Total weight

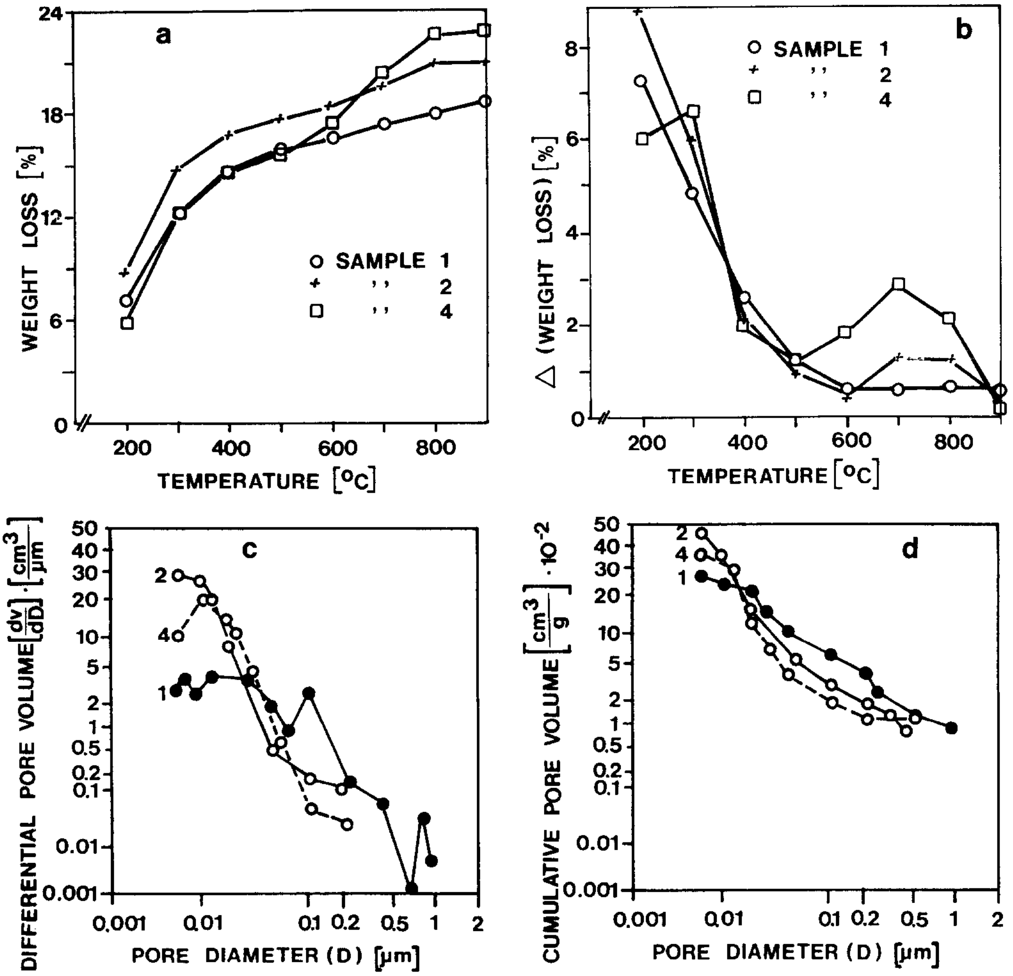

Fig. 3

Weight loss (a) and Δ[weight loss] (b) versus temperature and differential (c) and cumulative (d) pore volume versus pore diameter

loss is greater (fig. 3a) and especially pronounced up to 200°C (fig. 3b), thus implying the presence of amorphous C-S-H phases (12, 13). Greater weight loss between 700°C and 800°C (fig. 3b) is most likely due to larger extent of carbonation of sample No. 2 in comparison with sample No. 1 (14).

Figure 4 shows SEM micrographs of samples Nos. 1, 2 and 4. Sample No. 1 appears dense under the magnification of 10.000; rounded pores with a diameter from 0.5 to 1.0 um can be seen. Under the magnification of 50.000, rough-grained surface with 100 nm pores between grains are evident. There are also individual pores with diameter exceeding 200 nm.

Sample No. 4 appears dense under the magnification of 10.000, having individual pores of diameter of 200 nm. Magnification of 50.000 reveals fine-grained surface with the majority of spherical pores of the diameter of less than 30 nm and situated among the grains. Also present are long cracks 20 x 300 nm (D x L) and some 'c'-type (6) rounded pores with diameter of 200nm.

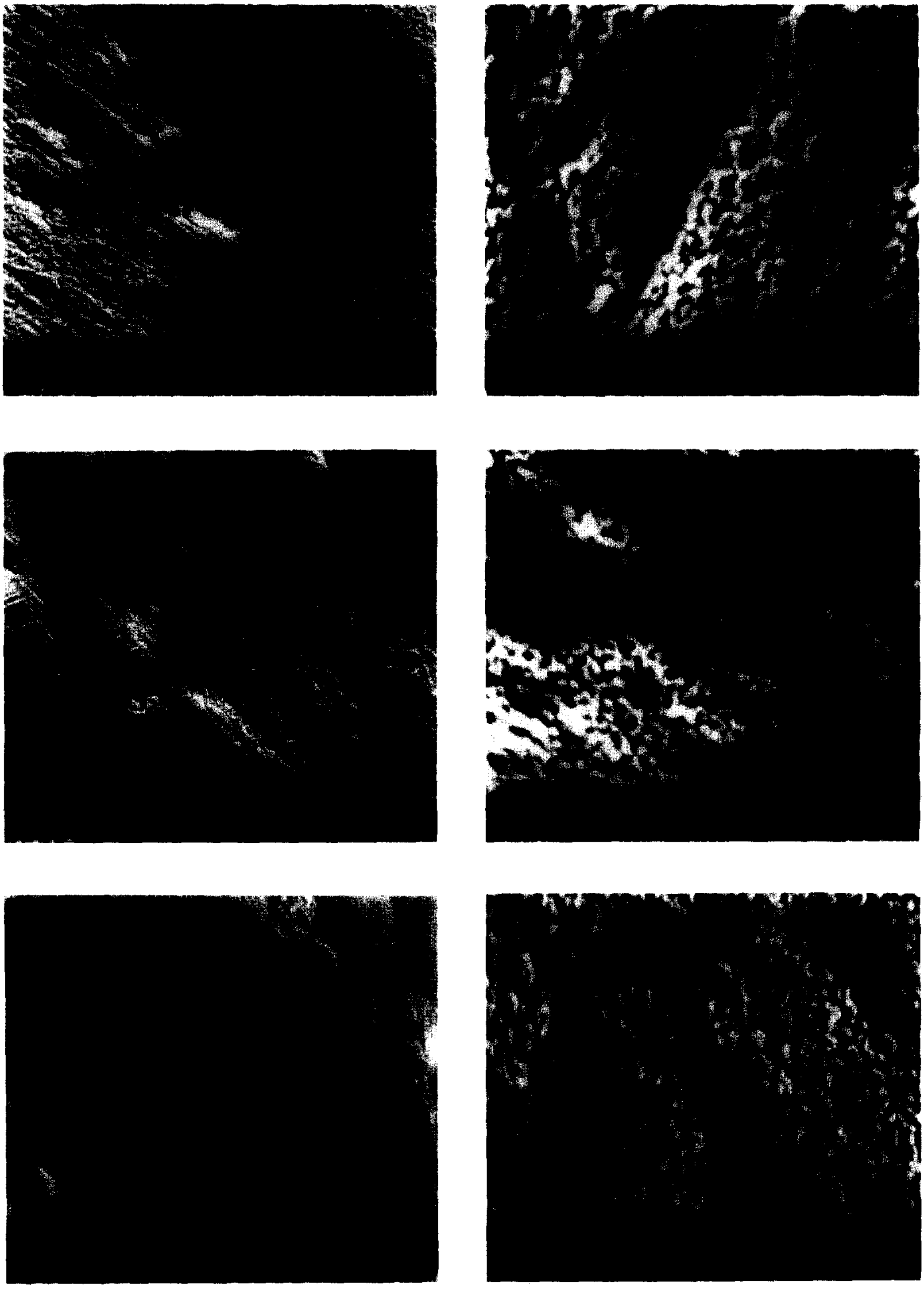

Fig. 4

SEM micrograph of pore shapes and pore size distribution

The formation of smaller pores, in comparison with sample No. 1, is related to the presence of 1.1 nm tobermorite (7) that also influences the increase of bending strength and elasticity. Quick breaking at maximum loading (fig. 2c) can be ascribed to the presence of pores of 'c'-type (6) that are also the cause of a somewhat increase in the toughness of the sample (fig. 2a).Sample No. 2 appears dense under the magnification of 10.000; shallow, regularly distributed cracks are distributed on the surface and there are no larger pores present. Under the magnification of 50.000 the surface of the sample appears smooth, comprised of agglomerates of different shapes and sizes that, although connected to each other, are nevertheless partly separated from each other by the crack-like pores with diameter of 20 nm. Within the agglomerates there are numerous small pores of various shapes with the diameter of less than 10 nm.

Porosity and pore size distribution as determined by MIP are given as cumulative and differential pore volume curves with regard to the pore diameter (figures 3c and 3d); bulk densities and total porosities are given in table 1.

Table 1
Bulk Density and Total Porosity

Sample Number	Bulk Density (kg/m^3)	Total Pore Volume (%)
1	1300	34
2	1290	48
4	1200	46

Samples No.1, No. 2 and No. 4 have the majority of pores between 30 and 70 nm, 10 and 30 nm and 6 and 30 nm, respectively. Maximum values of dV/dD are at 30, 10, and 6 nm for samples Nos. 1, 4, and 2, respectively (fig. 3 c).

Pores of larger diameters that usually appear between cellulose fibers and matrix in ACFRCC (4) are present in samples Nos. 4 and 2 in a significantly smaller amount than in sample No. 1. We can therefore conclude that a bond between cellulose fibers and matrix is better than in the unmodified product. Higher total porosities for samples Nos. 2 and 4, if compared to sample No. 1, and taking into the account small differences in bulk densities (Table 1), show greater influence of pore size distribution rather than of total pore volume (5) on bending strength, bending toughness and module of elasticity if the differences in phase composition are also taken into the account.

Conclusions

The effect of addition of either 26 wt.% of SWG and 10 wt.% of calcite or 5 wt.% of $CaCl_2$ on the starting mixture comprising 92 wt.% of Portland cement with sand (60:40) and 8 wt.% of cellulose fibers was studied on autoclaved products, treated for 6 hours at 180^oC under saturated steam conditions and dried for 6 hours at 105^oC.

The addition of 26 wt.% of SWG and 10 wt.% of calcite resulted in increased degrees of conversion of SiO_2, C_3S and C_2S and in larger amount of 1.1 nm tobermorite. Total porosity of products increased; the fraction of pores with the diameter of less than 30 nm increased also. The above addition resulted in higher bending strength and bending toughness, 20.0 MPa and 2.9 kJ/m^3, respectively, than in the product obtained without additions for which the corresponding values are 16.3 MPa and 1.6 kJ/m^3, respectively. There was a decrease in the fraction of larger pores and the module of elasticity decreased from 11.2.10^4 MPa for the product without additives to 4.7 . 10^4 MPa for the product containing SWG and calcite.

The addition of 26 wt.% of SWG and 5 wt.% of $CaCl_2$ resulted in changes that were largely similar to corresponding changes in the products with added SWG and calcite. Significant differences were, however, observed in the increased fraction of crack-like pores with the diameter of less than 10 nm and in the large increase of bending toughness to 8.9 kJ/m^3 as compared to 2.9 and 1.6 kJ/m^3 for samples containing either SWG and calcite or no additives, respectively.

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