Utilization of By-Product Waste Silica in Concrete–Based Materials

Danute Vaičiukynienė[a]*****, *Vitoldas Vaitkevičius*[a], *Aras Kantautas*[b], *Vytautas Sasnauskas*[a]

[a]*Faculty of Civil Engineering and Architecture, Kaunas University of Technology Studentų g. 48, LT – 51367 Kaunas, Lithuania*
[b]*Faculty of Chemical Technology, Kaunas University of Technology Radvilėnų str. 19, LT – 50254 Kaunas, Lithuania*

The usage of waste silica from AlF_3 production is limited due to admixtures of fluoride in its composition. The negative effect of admixtures was eliminated by thermally activating this silica gel. After thermal activation the mineralogical composition of silica gel changes. Fluorine is binding in low-reactive compounds, which insignificant effect on the cement hydration process. The possibilities of using waste by-product silica in hardened cement paste were investigated. Silica gel could be used as additive of the hardened cement paste after thermal activation (1 hour at 800 °C temperature). It was discovered that the optimum content of thermally activated technogenic silica gel additive under the conditions explored was up to 10% of the total quantity of the cement. After 28 days of hardening, the strength of hardened cement paste increased 7 MPa when the quantity of the additive was – 10% of the total weight when compared to the strength qualities of the samples with no additives used.

Keywords: *by product waste silica, concrete – based materials, AlF_3 production wastes*

1. Introduction

Phosphorites are decomposed by sulphuric acids in the production of phosphatic fertilizers. The reaction produces phosphoric and silicon hexafluoride acid, which, under the action of aluminium hydroxide, apart from the main product, i.e. aluminium fluoride, results the by-product silica gel $SiO_2 \cdot nH_2O$. The usage of this silica gel is limited due to the presence of aluminium fluoride in its composition. The negative effect of fluoride admixtures was eliminated by thermally activating the silica gel.

High purity silica is obtained by the reaction of impure waste by-product silica with hydrogen fluoride, producing silicon tetrafluoride gas and mother liquor[1]. The process is used for converting silicon and fluorine-containing waste gases into silicon dioxide and hydrogen fluoride[2]. A method for producing fumed silica and a fluorine-containing product from a source of silica in solid form was developed[3].

Results of studies on applications of silica waste – a by-product of fluorine processing – as fillers for rubber mixtures, rubber vulcanizates and urethan elastomers are available. A procedure for utilizing silica by-products from aluminium fluoride production was developed in this research[4,5].

The possibilities of producing binding materials by using waste product of AB *Lifosa* from the AlF_3 (silica gel) industry were investigated[6]. The influence of the composition of mixes (lime and waste products) and the conditions of the hardening process on the physical and mechanical properties of samples was analyzed. The optimal composition of lime, AlF_3 waste product and phosphogypsum mix was determined. The results of

experiments confirmed the possibility of utilizing these waste products for the production of binding materials.

The synthesis of low-temperature zeolites is presented[7]. For this synthesis it is possible to use this waste product (AlF_3 production waste from Kedainiai and granulated silica fume from Norway) instead of reagent silica gel. Crystal zeolite – hydrosodalite has been synthesized using these silica gels. When using AlF_3 production waste after 2 hours of isothermal exposure and the molar ratio of $Na_2O : Al_2O_3 : SiO_2 : H_2O = 2 : 1 : 2 : 10$ hydrosodalite has been crystallized and sodium fluoride formed, which, when necessary, can be washed out.

In this study[8], the effects of processes, in which the repeatedly recycled coarse aggregate absorbed the colloidal silica solution as pozzolanic liquid, on the properties of concrete were investigated. The absorbed colloidal silica solution is assumed to fill the micro cracks of the aggregate and to change to C-S-H by pozzolanic reaction. With this technique, the strength of repeatedly recycled aggregate concrete was enough to construct ordinary concrete structures, and the capacity of shear transfer at the interface along diagonal tension cracks was improved.

Since most of the analysed silica gel is composed of amorphous SiO_2, this silica gel acts in a similar manner as silica fume added in concretes and hardened cement paste. Direct tensile strength of hardened cement paste and mortar containing silica fume was evaluated at various water-cement ratios[9]. The results show that partial replacement of cement by 8% of silica fume resulted in higher tensile strength of the mortar, but showed no effect on the tensile strength of the cement paste. The replacement of cement by higher content

*e-mail: danute.palubinskaite@ktu.lt

of silica fume (16% and 25%) resulted in a decrease in the tensile strength of both the cement paste and the mortar.

The results[10] indicate that silica fume content does not significantly influence plastic shrinkage and settlement at investigated conditions. Another important observation was an immediate respond on external drying, which involves a low tensile strain capacity. The strain capacity seems to depend on the measured pore water pressure, which reflects the tensile stress in the pore water. The effect of silica fume content was not pronounced except for the sample with 15% admixture which showed a significantly higher rate of pressure drop than other concretes.

The authors have also established[11,12] that silica fume reacts with most of the $Ca(OH)_2$ formed during hydration within 28 days and improves the compressive strength of the mortar. Silica fume accelerates the hydration of $3CaO \cdot SiO_2$ (C_3S), reduces the amount of calcium hydroxide by reacting with it, and slightly lowers the $(1.5–2.0)CaO \cdot SiO_2 \cdot nH_2O$ (C–S–H) ratio of the C–S–H formed by hydration. Silica fume is considered a good model for reactive pozzolans used in concrete.

The results of the analysis[13] also show that the increase in compressive strength of mortar containing silica fume, as a partial replacement for cement, greatly contributes to strengthening the bond between the cement paste and the aggregate. Partial replacement of cement by silica fume and the addition of superplastisizer increase the strength of the mortar but have no influence on the strength of the cement paste.

Previous studies of M. Ilić et al. and A. Kutkaitis et al.[14,15] have shown that dried silica gel prevents cement hydration and strength of the samples is reduced compared to standard samples.

M. Ilić et al.[14] repot that the waste amorphous silica obtained from AlF_3 production could be used as additive in cement production. Experiments show that optimal quantity for the amorphous silica addition is 5% of the cement mass, but with this addition compressive strength was decreased, compared to standard sample.

The aim of this paper is to investigate the possibilities of using by product waste silica in hardened cement paste.

2. Material and Methods

2.1. *Materials*

The Portland cement CEM I 52.5 R (specific surface – 370 $kg.m^{-2}$, paste of normal thickness – 27.3%, initial setting time – 130 minutes, final setting – 215 minutes) was used this study.

Silica gel dried at 100 °C and thermally activated at 800 °C with the composition showed in Table 1. Chemical composition of Portland cement showed in Table 1.

2.2. *Methods*

The X-ray diffraction analysis using DRON – 6 diffractometer was conducted. The investigation was carried out with a 2Θ angle range 4 - 70° with Ni - filtered CuKα radiation. Thermographic investigations were carried out by using differential scanning calorimeter *STA 409 PC*

manufactured by *Netzsch*. The maximum temperature was 1500 °C, and the velocity of the increase in temperature was 10 °C/min. IR spectra were recorded with Perkin Elmer FT-IR System spectrometer. For the IR analysis, 1 mg of the substance was mixed with 200 mg of KBr and compressed in a forming press under vacuum. Particle size distribution and specific surface area were determined by "Mastersizer 2000" instrument from Malvern. Red light was produced by helium-neon laser and blue light was obtained from a solid phase source. The measuring principle was used Mie scattering analysis. A high resolution scanning electron microscope FEI Quanta 200 FEG with a Schottky field emission *gun* (*FEG*). Chemical compositions of modified AlF_3 production waste were investigated by an energy-dispersive X-ray spectrometer (EDS) with silicon type drift droplet detector.

For the analysis of the effect of silica gel addition (5, 10, 15% of mass) on the properties of cement concrete, the series of cement paste mixtures were chosen and mixed in a laboratory. Samples were formed, i.e. prisms of 4 × 4 × 16 cm in size, that hardened for 28 days. The compression strength of hardened cement paste was evaluated based on EN 196-1 standard. An automated and computerized ToniTechnik 2020 press was used to evaluate the compression strength of hardened cement paste.

3. Results and Discussion

The temperature of thermal activation (800 ± 3 °C) was chosen according of the results of thermal analysis of silica gel (Figure 1). The results showed that $AlF_3 \cdot 3.5H_2O$ loses three molecules of crystallization water at 187 °C. In the temperature range from 187 to 734 °C $SiO_2 \cdot nH_2O$ gradually dehydrates. At 734 °C AlF_3 completely loses hydration water. With the further increase of temperature, $SiO_2 \cdot nH_2O$ and AlO(OH) dehydrate. The total ignition loss up to 1000 °C was 41.33%.

The X-ray diffraction analysis showed that dried silica gel (Figure 2a, Cr. 2) contained amorphous $SiO_2 \cdot nH_2O$, also $AlF_3 \cdot 3.5H_2O$ and AlO(OH). When silica gel was heated at

Table 1. Chemical composition % of Portland cement CEM I 52.5 R, dried and thermally activated silica gel.

Chemical composition	Portland cement clinker	Thermally activated silica gel	Dried silica gel
SiO_2	21.00	60.15	60.54
Al_2O_3	3.90	4.43	-
AlF_3	-	35.52	-
AlO(OH)	-	-	2.99
$AlF_3 \cdot 3.5H_2O$	-	-	36.47
Fe_2O_3	2.90	-	-
CaO	66.00	-	
SO_3	3.40	-	-
Cl^-	0.06	-	-
MgO	2.70	-	-
C_3S	50.7	-	-
C_2S	18.5	-	-
C_3A	9.7	-	-
C_4AF	14.2	-	-

800 °C for 1 hour, its mineral composition changed: in addition to amorphous SiO_2, synthetic mulite $Al_{4.95}Si_{1.05}O_{9.52}$ and dehydrated AlF_3 were also formed. Chemical analysis results of dried silica gel showed in Table 1.

Figure 1. Thermal analysis of silica gel.

The negative effect of fluoride admixtures was eliminated by thermally activating this silica gel. After thermal activation the mineralogical composition of silica gel changes. Fluorine is binding in a low-reactive compounds: AlF_3 and $Al_{4.95}Si_{1.05}O_{9.52}$, which insignificant effect on the cement hydration process.

The strength of hardened cement paste specimens depends on the granular composition of the aggregates. The particle size and size distribution analysis has revealed that the diameters of silica gel particles are similar: in dried and thermally activated silica gel waste range from 79.4 to 91.20 μm (Figure 1b). However, the specific surface area was a slightly increased for thermally activated silica gel. The specific surface area for dried silica gel was $S = 0.27$ m^2. cm^{-3}, and for thermally activated silica gel $S = 0.39$ m^2.cm^{-3} corresponding to an average particle size.

The influence of dried silica gel on the strength of the hardened cement paste was investigated. It was determined
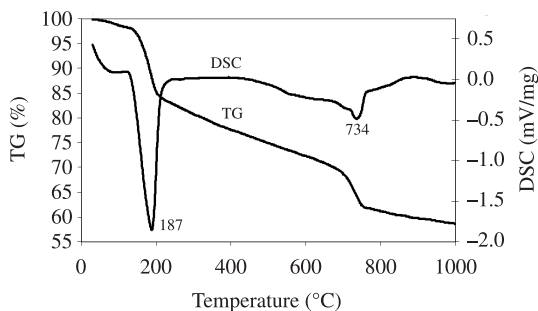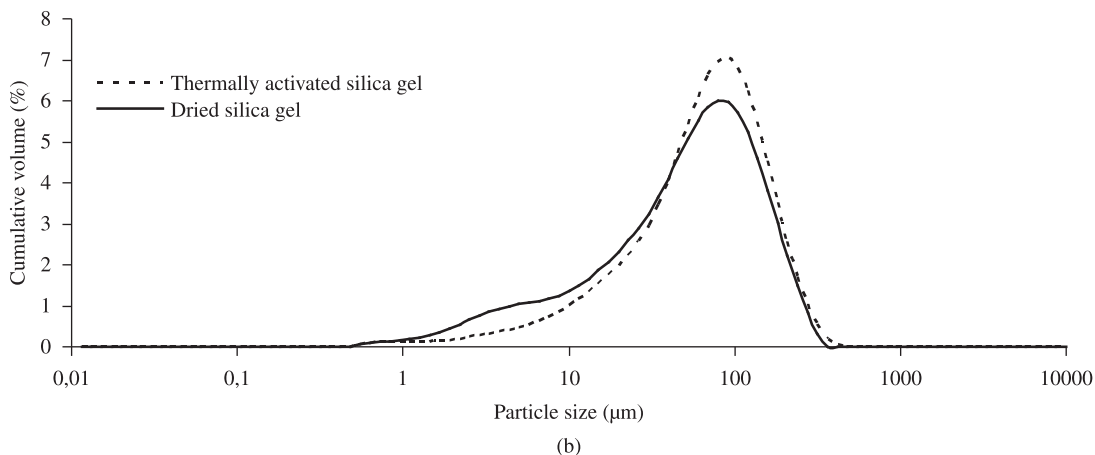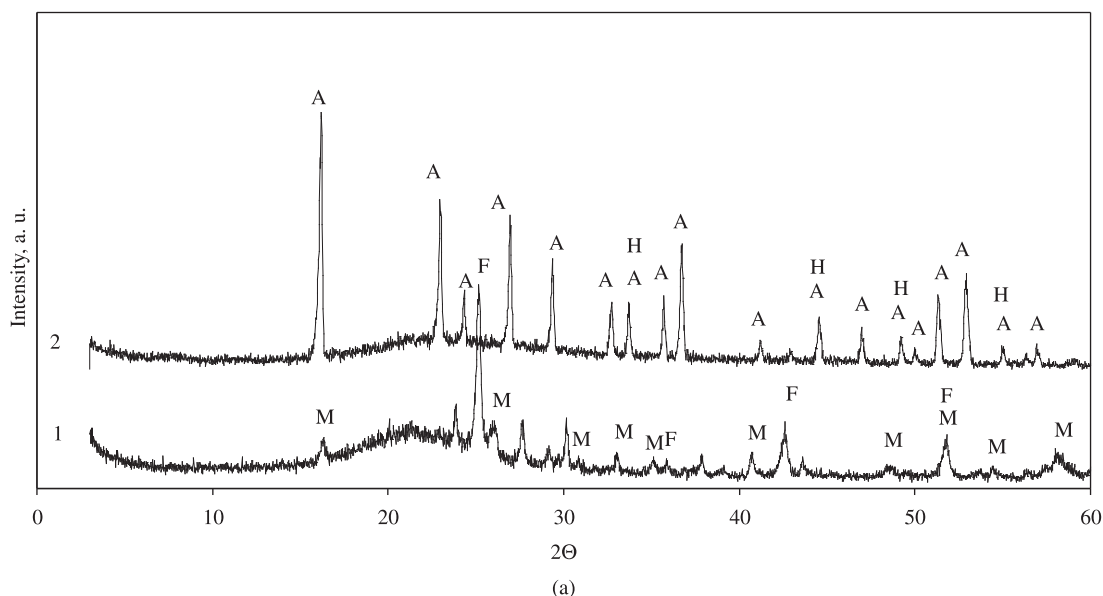

(a)

(b)

Figure 2. Distribution of silica gel particles (a) and X-ray diffraction patterns of silica gel (b): 1 – test sample thermally activated for 1 hour at 800 °C; *2* – test sample dried at 100 °C. *Notes – A – $AlF_3 \cdot 3.5H_2O$; M – $Al_{4.95}Si_{1.05}O_{9.52}$; F – AlF_3; H – AlO(OH).

that samples with a larger amount of this silica gel were weaker (Figure 3). For example, the compression strength of the samples with 15% of dried silica gel in hardened cement paste after 28 days decreased about 33 MPa when comparing to the specimens without any additives. These result confirmed the literature data[14,15], that dried silica gel prevents cement hydration and strength of the samples is reduced compared to standard samples.

The characteristics of silica gel changed substantially after they were thermally activated. It was determined

that the 10% addition of thermally activated silica gel to the total amount of cement increased the strength of the samples about 7 MPa when compared to the samples without additives (Figure 3). When the quantity of activated silica gel was increased more than 10%, the strength decrease. The strength of the samples that contained 15% of silica gel and hardened for 3 days was 2.5–5 MPa bigger when compared to the control samples.

Afterwards, the samples that contained only thermally activated silica gel were investigated.

Thermogravimetric analysis (Figure 4) of hardened cement paste showed that when the quantity of silica gel was increased from 0 to 15%, the quantity of $Ca(OH)_2$ in the mineral composition of the hardened cement paste decreased from 7 to 5 mg.g^{-1} respectively when the sample had been hydrated for 3 days; and from 18 to 11 mg.g^{-1} after 28 days of hydration. The analysis of X-ray diffraction patterns showed that the peaks of 0,493 nm inter-plane distances of $Ca(OH)_2$ were more intensive when no admixture was used, whereas less intensive peaks were noticed when 15 percent of silica gel admixture had been used (Figure 5).

After 3 days of hydration (Figure 4) of samples without admixture, calcite phase appeared as a secondary reaction of $Ca(OH)_2$ with atmospheric CO_2. The quantity of calcite decreased or it did not form in the samples where the admixture of silica gel was used and the samples were hardening for 28 days.

Thermographic analyses (Figure 4) showed that endothermal peaks of DSC curves for the temperature range between 100 and 200 °C indicated the elimination of water at C-S-H phase[16]. The second intensive endothermic peak for
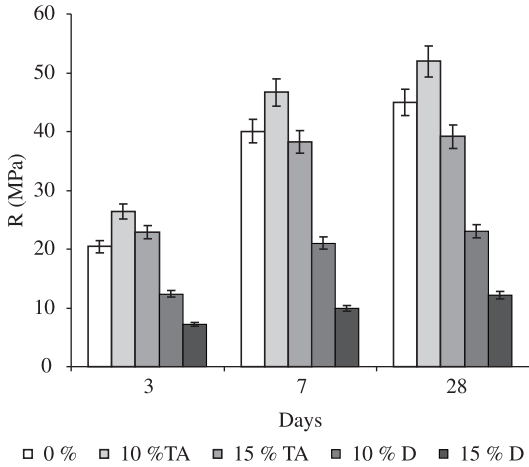

Figure 3. The dependence of hardened cement paste and compression strength on the amount of the silica gel admixture used. *Notes – D – dried silica gel; TA - thermally activated silica gel.
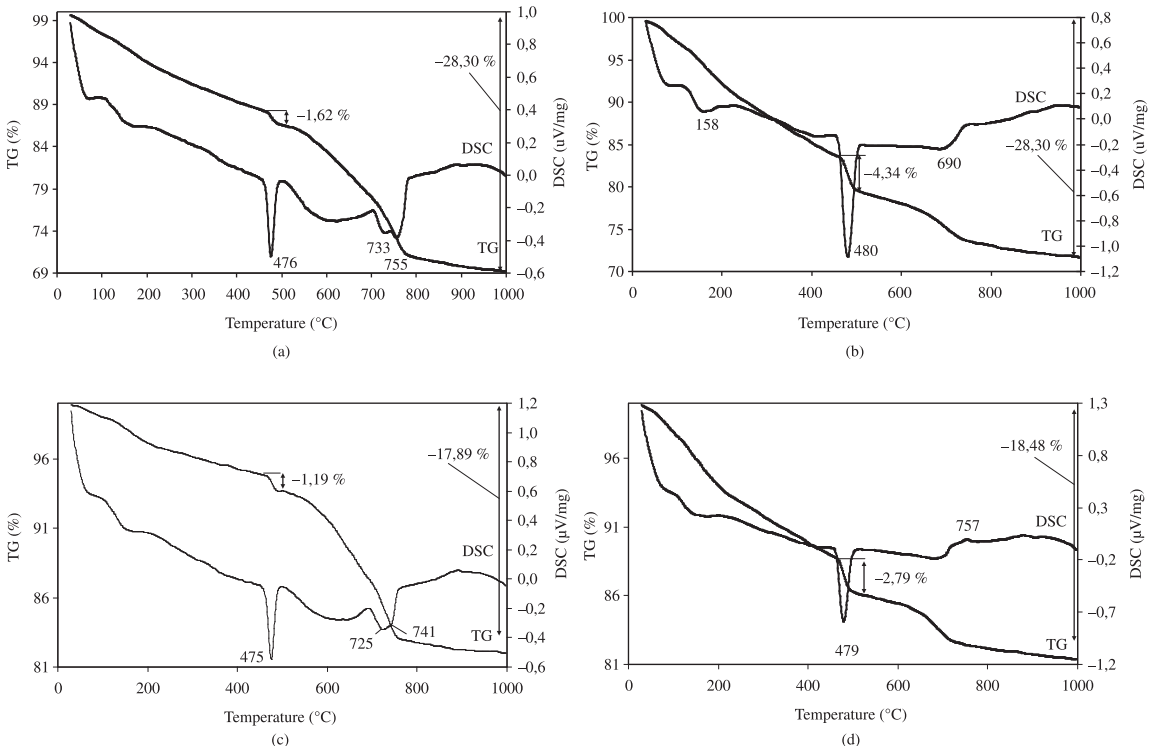

Figure 4. Thermograms of the hardened cement paste after the curing time for 3 (a, c) and 28 (b, d) days without (a, b) and with 10% (c, d) of thermally activated silica gel addition.
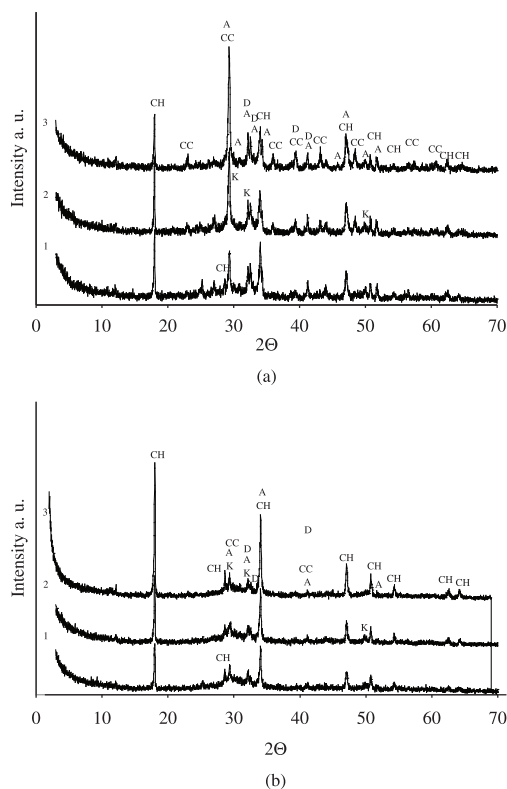
Figure 5. X-ray diffraction patterns of hardened cement paste after 3 days (a) and after 28 days (b) containing: 1 – 15%; 2 – 10% and 3 – 0% of silica gel. *Notes: CH – portlandite; A – alite; K – calcium silicate hydrate; D – belite; CC – calcite.
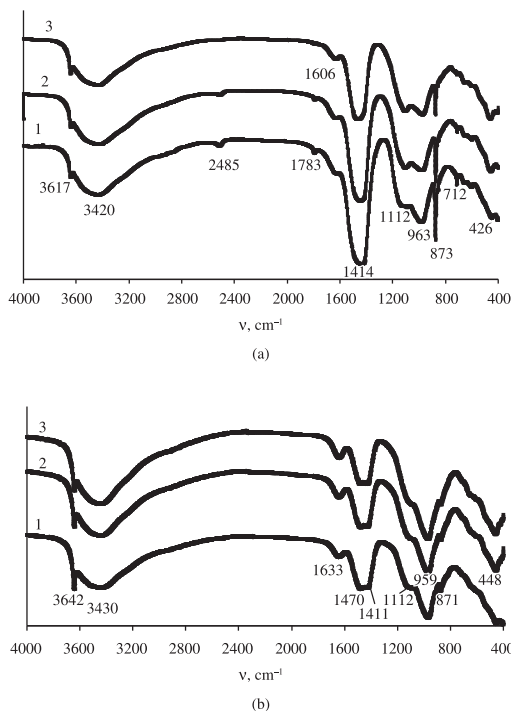

Figure 6. The FT-IR - spectra of hardened cement paste after 3 days (a) and after 28 days (b) containing: 1 – 0%; 2 – 10% and 3 – 15% of silica gel.

the temperature range between 475 and 480 °C indicated the dissociation of portlandite $Ca(OH)_2$[17,18]. Endothermal peaks for the temperature range between 690 and 733 °C can be attributed both to $CaCO_3$ decomposition and indicated the dehydration of calcium hydrosilicate which was similar to tobermorite at C-S-H phase. The exothermal peaks for the temperature range metween 750 and 757 °C attributed to the $CaCO_3$ decomposition[16,18].

In the range between 3100-3700 cm⁻¹, the H_2O and OH stretching bands appeared. IR spectra of the samples of hardened cement paste (Figure 6) with well-defined wide band of absorption in the 3420-3430 cm⁻¹ area indicated fluctuation and deformation of – OH hydroxyl group that belonged to intermolecular hydrogen bonds. A narrow band of absorption in the 3643-3644 cm⁻¹ area indicated – OH fluctuations of $Ca(OH)_2$ portlandite[19]. The quantity of silica gel used in the samples influenced the quantity of portlandite. When silica gel was not used in the samples a small increase of the OH⁻ band, associated with $Ca(OH)_2$ molecules, was recorded in the range between 3643 and 3644 cm⁻¹ when compared to the samples when silica gel was used.

The absorption bands in the 2517; 1796; 1447 and 875 cm⁻¹ areas of the spectrum were common to the fluctuations of carbonates of calcium carbonate[19]. It is possible to state that the quantity of $CaCO_3$ in the hardened cement paste decreased when the admixture was added as the intensity of absorption bands were directly proportional to the concentration of these groups. With admixture added all $CaCO_3$ peaks decreased proportionally, especially the band of absorption in the 875 cm⁻¹ area. When the maximum quantity of 15% of admixture had been added, the bands of absorption in the 2517 and 1796 cm⁻¹ area disappeared. The decrease in the quantity of $CaCO_3$ in the samples with silica gel admixture was more intense after 3 days of hydration. After 28 days of hydration $CaCO_3$ joined the structure of calcium hydro silicates, and carboxylates were formed[20].

The most intensive bands of absorption were observed in the range between 971-988 cm⁻¹. These absorption bands attributed to atomic frequencies of (Si, Al) - O bond in tetrahedron along the lines that bind $[(Si, Al)O_4]^{-4}$ tetrahedron oxygen atom with central Si or Al atom.

Ettringite formation was identified from the peaks in the range of 3420-3430 and 1112 cm⁻¹ area of absorption, and these vibrations were identified as S–O vibrations. Peaks pointing to the early formation of ettringite at the range of ~1122 cm⁻¹ were detected after 3 days of hydration.

It was proved that thermally activated silica gel acted as an active mineral addition; it also reacted with calcium hydroxide and formed a stable C-S-H form of calcium hydrosilicate (Figure 7). The established hydraulic activity of silica gel was 108 mg CaO/g. The SEM picture of the hardened cement paste with 10% of admixture used revealed needle crystals of calcium hydrosilicates. This observation suggests that this admixture forced the formation of calcium hydrosilicate.

In conclusion, it can be stated that part of concrete in concrete products can be replaced by thermally activated silica gel and this admixture actively participates in the process of hardened concrete paste hydration.
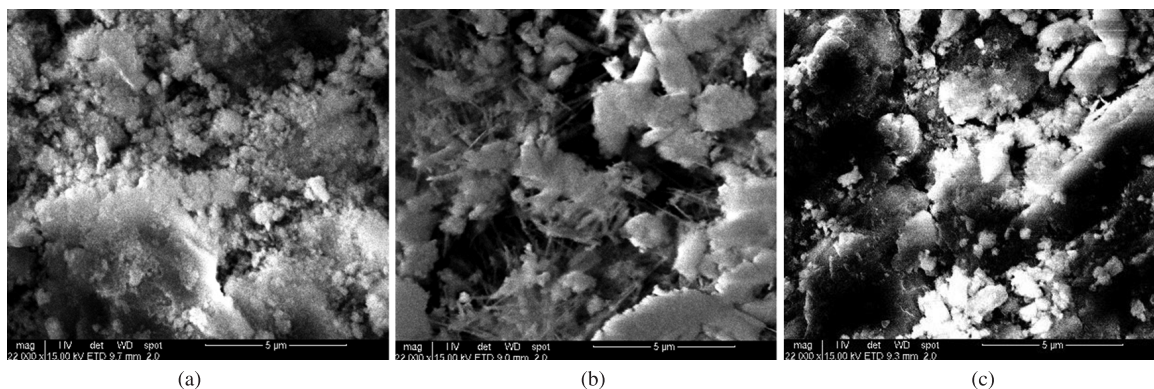
| (a) | (b) | (c) |

Figure 7. SEM of hardened cement paste containing 0% (a), 10% (b) and 15% (c) of silica gel.

4. Conclusions

From the research presented herein, the following conclusions can be derived:

- The negative effect of fluoride admixtures can be eliminated in AlF_3 production waste by thermally activating this silica gel. After thermal activation the mineralogical composition of silica gel changes. Fluorine is binding in a low-reactive compounds, which insignificantly effect on the cement hydration process;
- It was experimentally confirmed that the thermally activated silica gel could be used as an additive in hardened cement paste. This amorphous SiO_2 reacted with $Ca(OH)_2$ and form (C–S–H) type calcium silicate hydrates that additionally strengthened the hardened cement paste;
- It was determined the quantity of $Ca(OH)_2$ decreased from 7 to 5 mg.g^{-1} after 3 days of hydration, and from 18 to 11 mg.g^{-1} after 28 days of hydration when the quantity of silica gel additive in the samples had been increased from 0 to 15%; and
- After 28 days of hardening, the strength of the hardened cement paste increased 7 MPa (with 10% additive), compared with the control specimen without additives. This quantity of silica gel additive enables to decrease the quantity of used cement.

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