

Using of Modified AlF_3 Production Waste in Cement-Based Materials

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The paper deals with the investigations of impure silicagel $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$, obtained as a by-product of phosphatic fertilizers production, in hardened cement paste. It was determined that silicagel is a suitable additive in hardened cement paste only when thermally activated for 1 hour at 800 °C. An amorphous SiO_2 of this additive reacts with $\text{Ca}(\text{OH})_2$ that was formed during cement hydration and composes hydrosilicates of $(1.5\text{--}2.0)\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ type that add additional strength to the samples. With the optimal amount of additive of 10 % the compressive strength of hardened cement paste samples increases by (5–7) MPa compared to the samples without additive. By forming hardened cement paste samples with thermally activated SiO_2 it is observed, that it form agglomerate structures. The plasticizer additive is used to destroy the agglomerates. It was established that the optimal amount of plasticizer is 1.2 % in examine conditions, because it obtained the increase in strength of samples and smooth hardened cement paste structure form.

Keywords: modified silicagel; AlF_3 production waste, cement-based materials; dispergation.

INTRODUCTION

SiO_2 microdust in concrete is used to replace part of cement and as a pozzolan admixture. Microdust combines with a free calcium hydroxide during pozzolan reaction and creates a stable form of calcium hydrosilicate, and thus capillary pores are filled. The proper amount of SiO_2 admixture in concrete reduces cement expenditures, and increases strength and density of the concrete. Due to reduction of capillary porosity the hardened cement paste becomes stronger and more durable.

The influence of SiO_2 microdust lies on the fact that during the reaction with $\text{Ca}(\text{OH})_2$ it forms a more stable and dense hardened cement paste. Hardened cement paste contains an active dispersive admixture that forms calcium hydrosilicates during the $\text{Ca}(\text{OH})_2$ reaction.

Research on utilization of SiO_2 microdust in concrete first was carried out in the Scandinavian countries and the USA [1–6].

Silica fume influences concrete diffusivity in several ways: 1) densifying the microstructure of the interfacial transition zone regions, 2) reducing the overall capillary porosity for a fixed degree of cement hydration, and 3) producing a pozzolanic C–S–H gel with a relative diffusivity about 25 times less than that of the C–S–H gel produced from conventional cement hydration. According to the results [7] silica fume is most efficient for reducing diffusivity in lower w/c ratio concretes (w/c < 0.4). In these systems, for moderate additives of silica fume (e.g., 10 %), the reduction in concrete diffusivity may be a factor of fifteen or more, which may substantially increase the service life of steel-reinforced concrete exposed in a severe corrosion environment.

The authors have also established [8, 9] that silica fume reacts with most of the $\text{Ca}(\text{OH})_2$ formed during

hydration within 28 days and improves the compressive strength of the mortar. Silica fume accelerates the hydration of $3\text{CaO} \cdot \text{SiO}_2$ (C_3S), reduces the amount of calcium hydroxide formed by reacting with it, and slightly lowers the $(1.5\text{--}2.0)\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ (C–S–H) ratio of the C–S–H formed by hydration. Silica fume is considered as a good model for reactive pozzolans used in concrete.

When using the additive of amorphous SiO_2 in the concrete technology, its morphology, size of pores and particles as well as degree of dispersion in various solutions is very important. Some of works analyzed the mentioned problems of amorphous SiO_2 [10–13].

The direct strength of silica fume cement paste and mortar were evaluated at various ratios of water-cementations content [6]. Results show that partial replacement of cement by 8 % of silica fume resulted in an increase in the tensile strength of mortar, but showed no effect on the tensile strength of cement paste. The replacement of cement by higher dosage of silica fume (16 % and 25 %) resulted in a decrease in the tensile strength of both cement paste and mortar.

When producing phosphatic fertilizers from phosphorites, apart from the main products, fertilizers and AlF_3 , a contaminated amorphous SiO_2 of AlF_3 (<7 %) is generated [14]. As the major part of the investigated silicagel is formed of amorphous SiO_2 is a similar reaction must take place and the use of silica fume additive in the concrete and hardened cement paste.

The aim of this paper is to determine the possibilities of use of impure silicagel in hardened cement paste and to define the impact of dispersion on the production waste AlF_3 and cement specimens' properties.

MATERIALS AND TESTING METHOD

In this work Portland cement CEM I 52,5R (specific surface (by Blaine) – 370 kg/m², paste of normal consistence – 27.3 %, initial hydrating time – 130 min.,

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final set – 215 min.) with the chemical composition: CaO = 62.90 %; SiO₂ = 20.10 %; Al₂O₃ = 6.80 %; Fe₂O₃ = 4.70 %; Na₂O = 0.11 %; K₂O = 1.04 %; MgO = 1.80 %; SO₃ = 2.13 %; ignition losses = 0.4 %; and mineralogical composition: C₃S = 50.7 %; C₂S = 18.5 %; C₄AF = 14.2 %; C₃A = 9.7 % was used. W/C ratio of cement paste was 0.34 in all mixtures.

Silicagel, with the chemical composition SiO₂·*n*H₂O = 53.20 %; AlF₃·3.5H₂O = 32.05 %; AlO(OH) = 2.62 %; H₂O = 12.13 % was used as a cement additive. Samples were dried at 100 °C and thermally activated at 800 °C temperature.

Ca(OH)₂ content was calculated from the thermal analysis TG curve (the change in 400 °C–500 °C temperature).

Silicagel dispersion and modifying the system “GLENIUM ACE 30” polycarbocyclic plasticizer agent was used.

The X-ray diffraction analysis was conducted using DRON-6 diffractometer. The investigation was carried out with a 2θ angle range 4°–70° with Ni-filtered the CuK_α radiation. The thermographic investigations have been carried out by using differential scanning calorimeter STA 409 PC of firm Netzsch. Maximal temperature was 1500 °C, and the rate 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.

While analyzing the influence of the strength on the hardened cement paste properties, series of hardened cement paste mixtures were selected and mixed in a laboratory. The compositions differed by the contents of pre-dispersed silicagel – 0; 10 and 15 %. The formed test samples, (4×4×16) cm sized prisms, were left to hydrating for 28 days under conditions prescribed by EN 12390-2 standard. Based on EN 196-1 standard, the compressive strength of hardened cement paste was measured. The compressive strength relative error did not exceed 0.3 %.

RESULTS AND DISCUSSION

The temperature of thermal activation (800 °C ± 3 °C) was chosen with regard to the results of thermographical analysis of silicagel (Fig. 1). The results showed that AlF₃·3.5H₂O loses three molecules of crystallization water at 187 °C. In the temperature range from 187 °C to 734 °C SiO₂·*n*H₂O gradually dehydrates. At 734 °C AlF₃ completely loses hydration water. With the further increase of temperature, SiO₂·*n*H₂O and AlO(OH) dehydrate. The total ignition loss up to 1000 °C was 41.33 %.

After the X-ray diffraction analysis, apart from the predominant amorphous SiO₂·*n*H₂O, the dried silicagel (Fig. 2) also contain AlF₃·3.5H₂O and AlO(OH), and upon heating it at 800 °C for 1 hour it changed its mineral composition: in additive to the amorphous SiO₂, the synthetic mulite Al_{4.95}Si_{1.05}O_{9.52} and dehydrated AlF₃ are also formed. Based on chemical analysis the dried silicagel contain 60.15 % of SiO₂, AlF₃ = 35.52 %, Al₂O₃ = 4.43 %. While analyzing the influence of dried silicagel additive on

the strength of hardened cement paste it was determined that the increasing amount of this additive in cement negatively affects the strength properties of the samples (Fig. 3). The compressive strength of the samples decreases when more additive is added. From the test results can be assumed that hydration during the formation of CaF₂ in react of AlF₃·3.5H₂O with Ca(OH)₂ adversely affects the strength of the samples [15]. The compressive strength decreases by 33 MPa after 28 days of hydrating with 15 % of the additive.

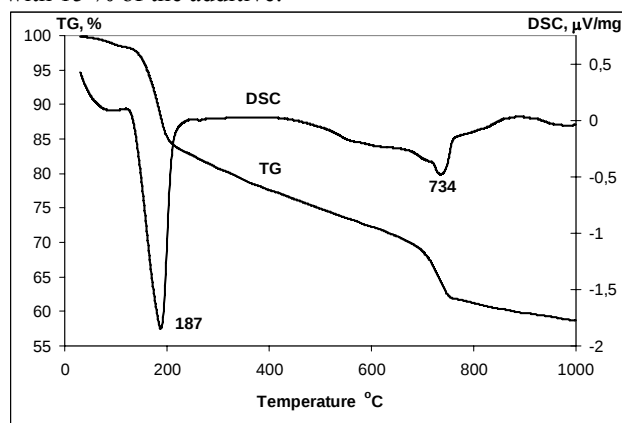


Fig. 1. Curves of thermal analysis of silicagel

Thermal activation of silicagel essentially changes not only chemical composition but its properties too. It was established that 10 % of thermally activated silicagel additive of the amount of cement increases the strength of samples by 6 MPa–7 MPa compared to those without the additive (Fig. 3). This consistent pattern with regard to the samples under compression is noticeable both after 3 days and after 28 days. With the increase of silicagel additive of more than 10 %, the strength of the samples starts to decrease. After 3 days of hardening the strength of the samples containing 15 % of silicagel additive is 2.5 MPa–5 MPa higher than the strength of the reference samples.

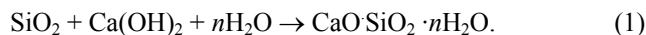
The analysis of X-ray diffraction patterns of hardened cement paste with the silicagel additive has shown that with the increase of this additive from 0 % to 15 %, the amount of Ca(OH)₂ in the mineralogical composition of hardened cement paste decreases from 1.80 % to 1.75 % after 3 days of hydration and from 4.44 % to 1.94 % after 28 days of hydration. Peaks of Ca(OH)₂ are more intensive without the additive, while peaks are less intensive (Fig. 4) with 15 % of additive. The observations of test sample hydrating duration have proved that the longer is the test sample hydrating duration (Fig. 4) the higher is the content of Ca(OH)₂ and the bigger part of 3CaO·SiO₂. Some parts of 2CaO·SiO₂ are transformed into calcium hydrosilicates and calcium hydroxide.

After 3 days of hydration (Fig. 4) and without the additive in the mineralogical composition of the samples, the CaCO₃ phase also appears as a result of the secondary reaction of Ca(OH)₂ with the atmospheric CO₂. However, when the samples are hardened for a longer period, i. e. 28 days, and upon applying the additive of modified silicagel, CaCO₃ is not formed.

From the obtained test results it can be said that thermally activated AlF₃ production waste acts as an active

mineral admixture; it reacts with free lime that is formed during the process of cement hydration. The bigger (more than 10 %) is the amount of AlF_3 production waste admixture, the lower is the strength of the test samples.

Thermally activated AlF_3 production waste additive actively participates in the process of hydration. This modified material combines with a free calcium hydroxide during the puzzolane reaction and forms a stable form of calcium hydrosilicate C–S–H. AlF_3 production waste admixture is reacting with Ca(OH)_2 and forms a more stable and denser cement stone.



The optimal quantity of thermally activated AlF_3 production waste additive (10 %) would reduce the input of cement in concretes and will reduce the excretion of free lime concrete products surface.

These findings prove the earlier research [16], using SiO_2 microdust wherein the set optimal amount of SiO_2 microdust fluctuates from 8 % to 10 % of the cement mass.

Endothermic peaks of these samples in DSC curves (Fig. 5) in the temperature range of 100 °C to 200 °C show the removal of water from tobermorite gel phase. The second intensive endothermic peak at the temperature range of 475 °C–479 °C shows the decomposition of portlandite Ca(OH)_2 . The endothermic peak at 725 °C temperature is related to the water removal from the tobermorite-like calcium hydrosilicate (1.5–2.0)

$\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$. $\beta\text{-C}_2\text{S}$ is formed at the mentioned temperature. Exothermal peak at 757 °C temperature show the transition of C–S–H to wollastonite.

The samples of the hardened cement paste were analyzed by using the IR spectroscopy method. Valence vibrations of O–H bond are one of the most typical in the infrared spectrum and form an intensive absorption band in the spectrum range of (3600–3200) cm^{-1} . The position and the nature of the absorption band depend on whether the hydroxigroup has a hydrogen bond.

In this work modified silicagel was investigated, which was formed from amorphous SiO_2 so similar influence on hardened cement paste must take place. The results of this study confirm previous findings [1–6]: silica fume reacts with most of the Ca(OH)_2 formed during cement hydration by composing (1.5–2.0) $\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ (C–S–H) type hydrosilicates that are adding some strength to the samples.

The clear and broad absorption bands are noticeable in the IR spectra of hardened cement paste samples (Fig. 6) in the range of (3431–3444) cm^{-1} and show the oscillations of OH hydroxigroups with the intermolecular hydrogen bond. The absorption bands in the area of (1624–1645) cm^{-1} show the deformation vibrations of water molecules. While narrow absorption bands in the range of (3643–3644) cm^{-1} show the OH vibrations of the Ca(OH)_2 portlandite [17].

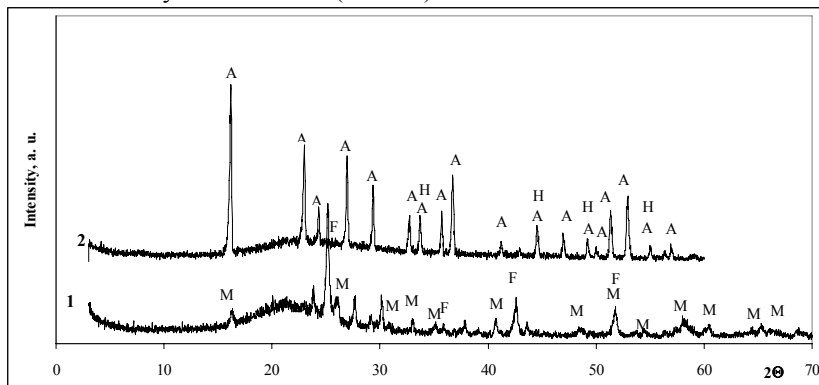


Fig. 2. X-ray diffraction patterns of modified silicagel: 1 – test sample thermally activated for 1 hour in 800 °C; 2 – test sample dried in 100 °C. *Notes: A – $\text{AlF}_3 \cdot 3.5\text{H}_2\text{O}$; M – $\text{Al}_{4.95}\text{Si}_{1.05}\text{O}_{9.52}$; F – AlF_3 ; H – AlO(OH)

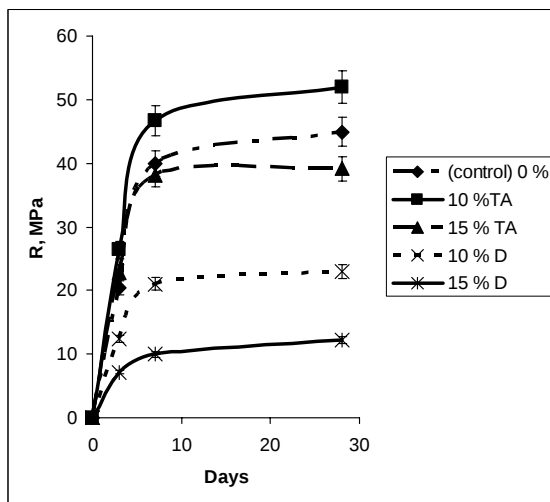
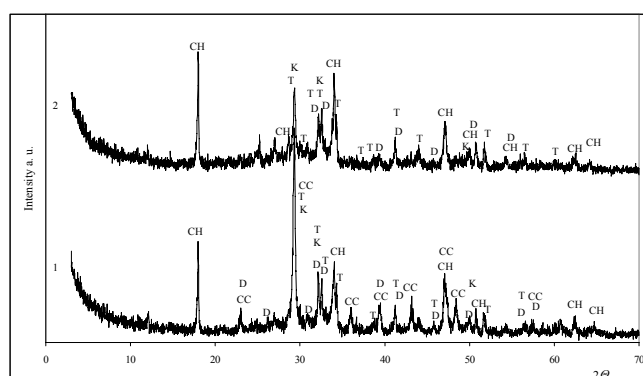


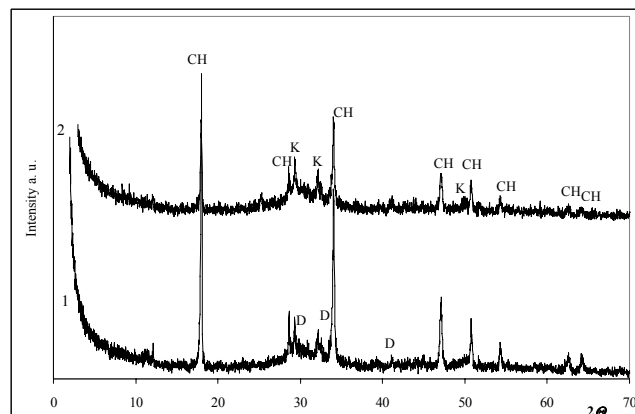
Fig. 3. The dependence of compression strength of hardened cement paste on the amount of the silicagel admixture used. *Notes: D – dried silicagel; TA – thermally activated silicagel

Absorption bands in the range of 2517; 1796; 1447 and 875 cm^{-1} are characteristic to CaCO_3 [18]. Since the intensity of absorption bands is directly proportional to the concentration of these groups, it is true to say that the amount of CaCO_3 decreases after adding the silicagel in the cement paste. All CaCO_3 peaks characteristic are proportionally decreasing after adding the additive, especially the band of 875 cm^{-1} , and with the maximum 15 % of the additive 2517 cm^{-1} and 1796 cm^{-1} absorption bands in the IR spectroscopy curves disappear. The mentioned decrease of CaCO_3 amount is due to the modified silicagel additive and it is seen only at the beginning of the process, i. e. after 3 days. After 28 days of hydration of the hardened cement paste CaCO_3 proceeds to the structure of calcium hydrosilicates and carboxylicates are formed [19].

A wide absorption band of 1000 cm^{-1} shows the vibrations of Si–O bond. All spectra contain absorption bands of the highest intensity which are of (1112–971) cm^{-1} . These absorption bands belong to the valence Si–O bond vibrations in tetrahedron along the lines connecting $[(\text{Si})\text{O}_4]^-$ tetrahedron atom with the central Si atom. There can be noticed a shift of frequency of valence Si–O vibrations to the range of lower frequencies, which may be related to the weaker Si–O bond in the structure.

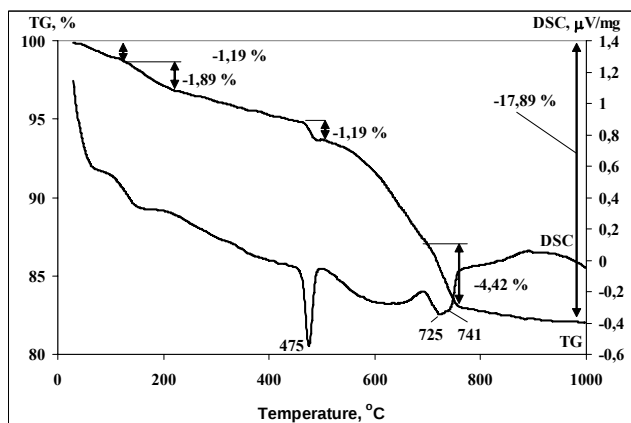


a

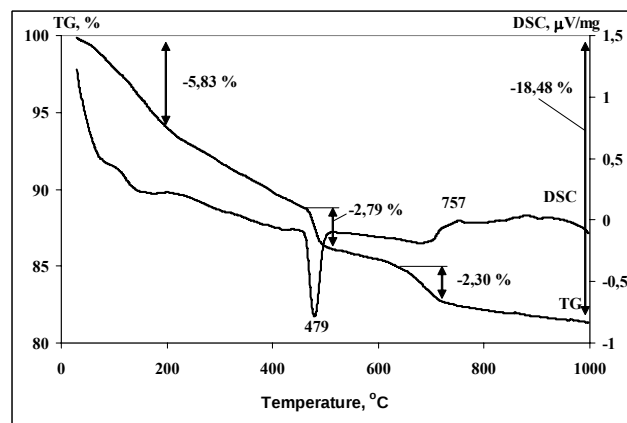


b

Fig. 4. X-ray diffraction patterns of hardened cement paste after 3 days (a) and after 28 days (b) containing 0 % (1) and 15 % (2) of modified silicagel. *Notes: CH – $\text{Ca}(\text{OH})_2$; T – $\text{Ca}_5\text{MgAl}_2\text{Si}_{16}\text{O}_{90}(\text{C}_3\text{S})$; K – C–S–H; D – $2\text{CaO}\cdot\text{SiO}_2(\text{C}_2\text{S})$; CC – CaCO_3



a



b

Fig. 5. The thermograms of hardened cement paste containing 10 % of modified silicagel: a – after 3 days; b – after 28 days

In this study it was proved that thermally activated silicagel acts as an active mineral additive, it also reacts with calcium hydroxide and forms a stable C–S–H form of calcium hydrosilicate. The established hydraulic activity was 108 mg CaO/g of silicagel.

On mixing concrete masses with an admixture (Fig. 7, a) of thermally activated silicagel (further referred to as modified silicagel) of AlF_3 production it was noticed that the admixture is poorly mixed in concrete mass and forms spongy inserts having no strength (Fig. 8, a). Therefore, this analysis aims to find out dispersion possibilities of the modified silicagel, how to obtain a concrete mass as homogenous as possible and how this influences strength properties of cement samples.

To obtain a homogeneous mass of cement the additive of liquid polycarboxylic plasticizer agent accounting for 1.2 % of the total mass of solid substances was used as recommended by the manufacturer. Due to electrostatic stabilization, its molecular structure forms a big surface for the particles participating in cement hydration. It was determined that this particular amount of the additive is fully sufficient to break the aggregation of the modified silicagel's particles (Fig. 7, b) and due to this the mixed cement mass becomes homogeneous and no accumulations of silicagel were detected in the cement stone (Fig. 8, b).

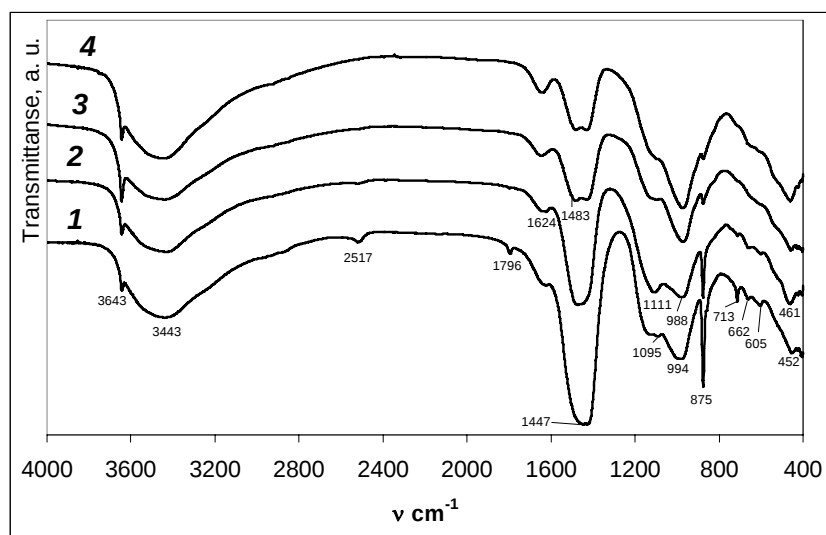


Fig. 6. The IR spectra of hardened cement paste containing 0 % (1, 3) and containing 15 % (2, 4) of modified silicagel: 1, 2 – after 3 days; 3, 4 – after 28 days

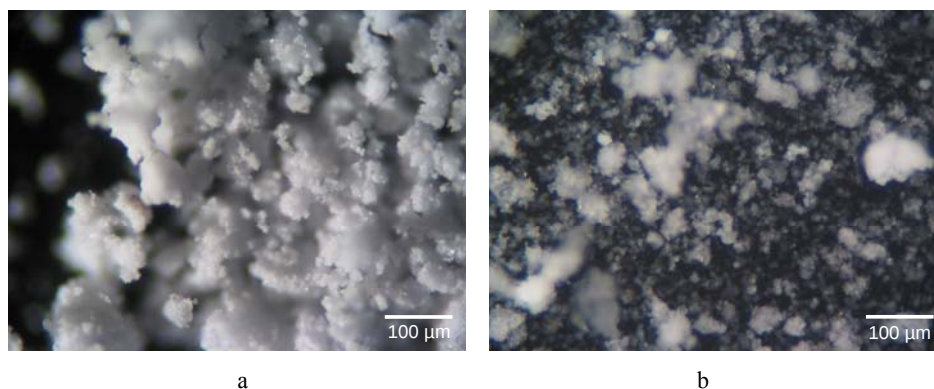


Fig. 7. A microscopic photograph of an AlF_3 production waste before (a) and after (b) the dispersion

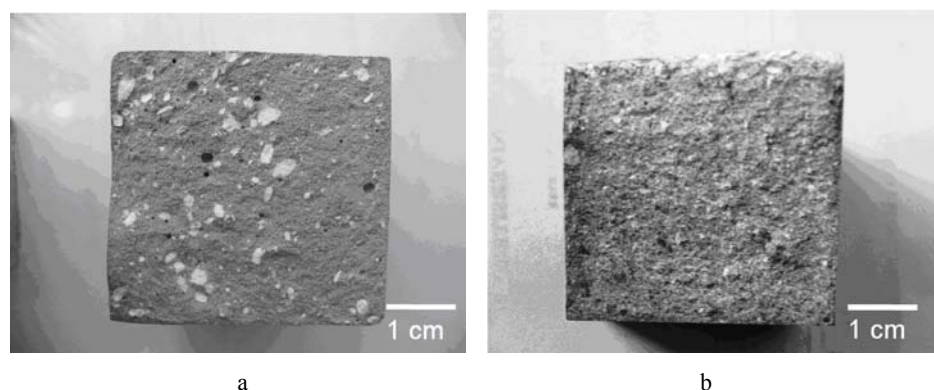


Fig. 8. Photos of hardened cement paste specimens when using non-dispersed (a) and dispersed (b) AlF_3 production waste

The analysis of compressive strength of the hardened cement paste showed that due to a plasticizer added to the cement paste without a modified silicagel admixture the samples had a higher strength with a plasticizer admixture after 3 days compared to the samples formed of the cement paste only (Fig. 9). This is because the plasticizer added to the cement paste causes not only the dispersion of the particles taking part in hydration but also a very rapid adsorption of plasticizer molecules on cement particles. These two effects influence the previous reactions of hydration. Heat relieved in these reactions is efficiently used which faster increases the strength of the cement in

the first days of hardening. However, the strength of all samples levels out after 28 days.

The analysis of the compressive strength of the hardened cement paste both with dispersed and non-dispersed admixture of AlF_3 production waste showed that a 10 % of dispersed admixture of modified silicagel increases the compressive strength to 4 MPa only after 28 days due to the better structure of the hardened cement paste compared to the samples formed with the same amount of undispersed admixture. 15 % of admixture of dispersed AlF_3 production waste increases the compressive strength of the samples both after 3 and after 28 days of hardening which

almost does not differ from compressive strength of the samples with the same amount of non-dispersed silicagel.

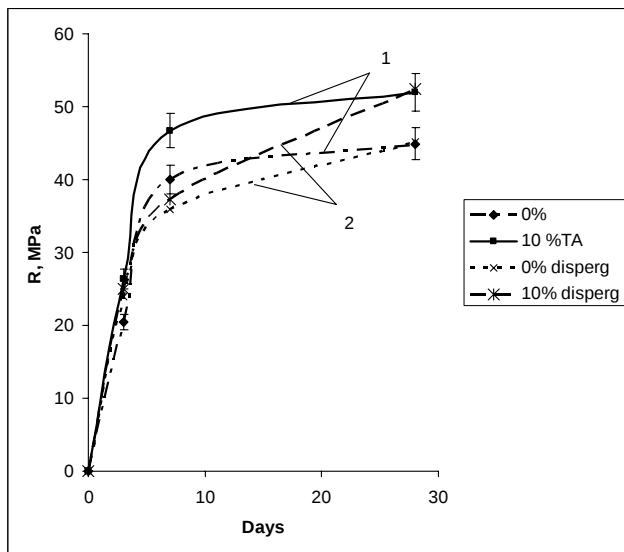
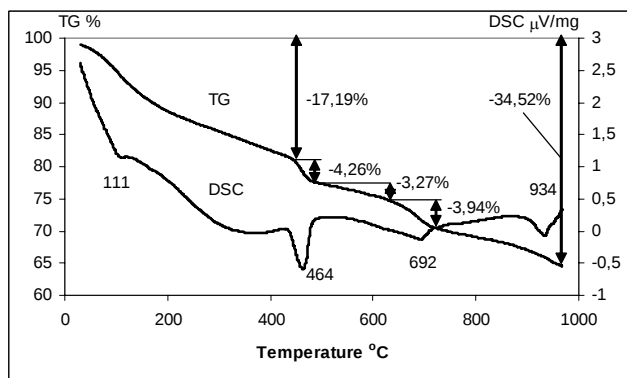
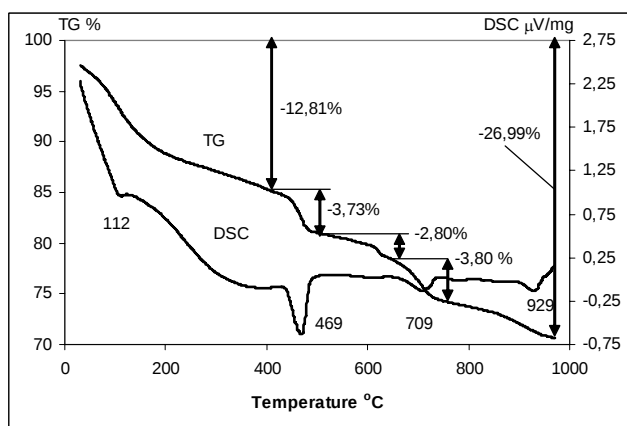


Fig. 9. The dependence of hardened cement paste and compressive strength on the amount of the silicagel and dispersed silicagel admixture used. *Notes 1 – silicagel and 2 – dispersed silicagel admixture used



a



b

Fig. 10. Thermograms of hardened cement paste after 28 days containing 0 % (a) and 10 % (b) of modified silicagel. The samples are formed with plasticizer (1.2 %)

The best results are obtained when using 10 % of the dispersed modified silicagel additive in the cement specimens. The additional strength increment in them is

obtained due to a more homogeneous distribution of silicagel in the hardened cement paste and the formation of new calcium hydrosilicates during chemical reactions between the Ca(OH)_2 evolved during hydration and the amorphous SiO_2 .

According to the DSC curves (Fig. 10) endothermal peaks from 100 °C to 200 °C of temperature indicate the removal of water from tobermorite gel phase. The second more intensive endothermal peak present in all DSC curves in the temperature of 462 °C–469 °C indicates the split of portlandite Ca(OH)_2 . The peaks in the temperature of 692 °C–709 °C are related to the removal of water from the tobermorite-like calcium hydrosilicate $(1.5\text{--}2.0)\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$. Endothermic peaks in the temperature of 934 °C–929 °C show the split of CaCO_3 . The most distinct peak of CaCO_3 is formed without the admixture, decreases with 10 % of admixture and disappears with 15 % of admixture. Thus, it can be presumed that CaCO_3 moves to calcium hydrosilicates and carboxylicates are formed.

To conclude the results, it can be stated that part of cement in cement products can be replaced by thermally activated modified silicagel and its additive actively participates in the process of hardened cement paste hydration.

CNCLUSIONS

The silicagel thermally activated for 1 hour at 800 °C temperature is suitable as an additive in hardened cement paste since the amorphous SiO_2 of this additive reacts with Ca(OH)_2 that is formed during cement hydration by composing $(1.5\text{--}2.0)\text{CaO}\cdot\text{SiO}_2\cdot n\text{H}_2\text{O}$ (C–S–H) type hydrosilicates that add some strength to the samples.

The additive of thermally activated silicagel reduces the Ca(OH)_2 content in hardened cement paste which forms new compounds of calcium hydrosilicates. With the increase of the amount of this additive from 0 to 10 %, the Ca(OH)_2 amount in the mineralogical composition of the hardened cement paste after 3 days of hydration decreases from 7.40 mg/g to 4.89 mg/g and from 18.25 mg/g to 11.47 mg/g after 28 days of hydration.

Based on the analyzed conditions, the most appropriate amount of thermally activated silicagel additive is up to 10 % of the used cement mass. With 10 % of the additive, the strength properties of the samples are improved by 6 MPa–7 MPa after 28 days of hardening compared to the strength properties of the samples without the additive. This amount of silicagel additive in concretes allows the reduction of cement input by replacing part of cement.

Similar results were obtained with the samples containing 10 % of the cement was replaced by the dispersed modified silicagel. The additional strength increment in them is obtained due to a more homogeneous distribution of silicagel in the hardened cement paste and the formation of new calcium hydrosilicates during chemical reactions between Ca(OH)_2 evolved during hydration and the amorphous SiO_2 .

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