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The Pozzolanic Activity of Calcined Clay – Silica Gel Composites

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The effect of silica gel additive on pozzolanic activity of burned clays was investigated on this study. It was determined that calcined (600 ºC – 730 ºC) clay of Saltiskiai quarry has very low pozzolanic activity (104 mg – 55 mg CaO/g). It was observed that during calcination process the fluorine ions from silica gel were not combined to another compounds but directly passed to atmosphere. Moreover, silica gel additive significantly increases the mentioned clay activity, which depends on the quantity of the used additive. It was determined that 10 % of silica gel additive increases the pozzolanic activity of composite with clay of Saltiskiai quarry up to 109 mg CaO/g, meanwhile the 80 % – unto 257 mg CaO/g. The same effect of silica gel additive was observed in the samples with Dukstyna quarry clay. It was found that the pozzolanic activity of Dukstyna clay-silica gel composite with 10 % of silica gel additive, burned at 600 ºC for 1h, was 7 % higher (168 mgCaO) than the activity of the clay samples (157 mgCaO/g), whereas 229 mgCaO/g pozzolanic activity was reached than 80 % additive of silica gel was used. Despite this fact, the pozzolanic activity decreases when the calcination at 700 ºC – 860 ºC temperature was carried out.

Keywords: clay, kaolinite, silica gel, composite, pozzolanic activity.

1. INTRODUCTION

A pozzolana is defined as (ASTM C125) "a siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form in the presence of moisture, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties" [1, 2].

Calcined clay is one of the earliest known pozzolanic materials [3] and depending on the pozzolanic activity of the calcined clays this material allows to replace a part of cement in concrete to improve long term strength and durability [4]. It is proposed, that the calcining temperature producing the active state is usually in the range of (600 – 800) °C [5], that causes destruction of crystalline structure of the clay and formation of amorphous silica and alumina [6]. Though, the compositions of clay minerals depend on geographic area and the bedrock, and vary a lot all over the world [5].

Donatello S. et al maintained [7] that pozzolanic activity arises from the reaction of amorphous silica with $Ca(OH)_2$ to form calcium silicate hydrate gel.

A new source of pozzolana could be a waste from aluminum fluoride industries – silica gel. The structure of the precipitated silica depends on many variables, including reaction temperature and time, concentration of reagents, structure of aluminum hydroxide used, purity of fluorosilicic acid [8], degree of impurities elution and washing technology of silica [9].

Producing 1 t of aluminum fluoride generally formed about 0.5 t of silica gel waste. Unfortunately, in some countries the technogenic silica gel, as concerning various impurities containing fluoride, is not widely used or processed and stored in a landfill site [10 – 12].

It is expected, that during burning of clay – silica gel composites, the pozzolanic activity of synthesis products will increase and aggressive fluorine ions on silica gel will be combined to CaF_2. This would solve the recovery possibility and consumption of waste, if products of synthesis could be used as pozzolanic additive on cementious motars.

The aim of this work was to determine the influence of silica gel on pozzolanic activity of calcined clay – silica gel composites.

2. MATERIALS AND METHODOLOGY

2.1. Materials

Chemical analysis and characteristics of the used dried raw materials are shown in Table 1. The XRD data of clays and silica gel are presented in Fig. 1 and Fig. 2 respectively.

2.2. Methods

Clays were chopped, dried at 100 °C ±2 °C temperature for 24 h and ground by laboratory dismembrator. Powder was sieved through the 0.3 mm mesh. Siftings were milled by roll mill. Both fractions were homogenized by ball mill for 45 minutes.

Silica gel (moisture 65 %) was dried at 50 ºC for 48 h.

Samples of dried silica gel was burned at 600, 700, 800, 900 °C temperature for 1 h. Heating rate of 10 ºC/min.

In order to determine the influence of the silica gel on pozzolanic activity of clay-silica gel composites, the granules (12 mm ±2 mm) were formed from the mixtures where 10, 20, 50, 80 % of dried waste were added. The water-to-solid (w/s) ratio of mixtures varied from 0.4 to 1.2. Granules were dried at 98 ºC temperature for 24 h and then burned at 600, 700, 730, 800, 860 ºC temperature for 1 h (10 ºC/min). After burning, samples were crushed by jaw crusher and ground by planetary mill for 40 seconds at 600 rpm.

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Table 1. Chemical composition and characteristics of raw materials

Parameter, wt. %	Clay of Saltiskiai quarry (Š)	Clay of Dukstyna quarry (D)
SiO_2	48.02	56.12
Al_2O_3	13.33	19.36
Fe_2O_3	6.69	7.78
CaO	10.19	0.88
MgO	4.59	2.09
K_2O	2.75	3.61
Na_2O	0.376	0.309
Loss on ignition	14.81	9.85
Content of carbonates	18.02	1.64
Content of kaolinite	2.97	10.09

Parameter, wt. %	Silica gel (S)
SiO_2	77.77
F^-	8.64
Al^{3+}	4.03
Loss on ignition	9.56
Specific surface area, m^2/kg	400

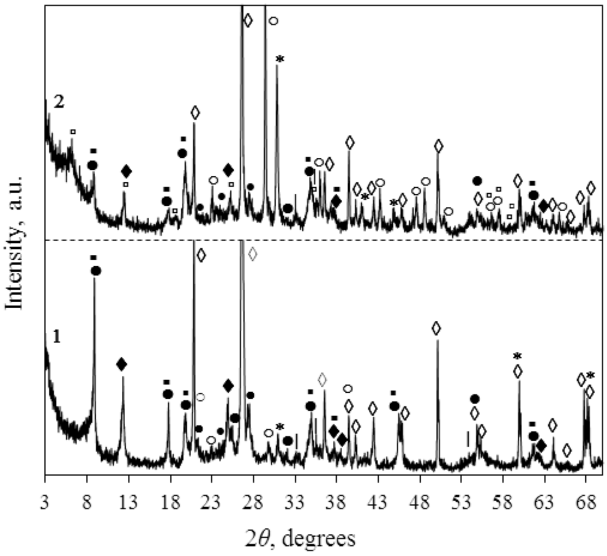


Fig. 1. X-ray diffraction patterns of clays: 1 – Dukstyna quarry; 2 – Saltiskiai quarry. Indexes: ♦ – kaolinite; ● – illite; ▪ – muscovite; ◊ – quartz; ○ – calcite; * – dolomite; • – feldspa; | – hematite; ▫ – chlorite

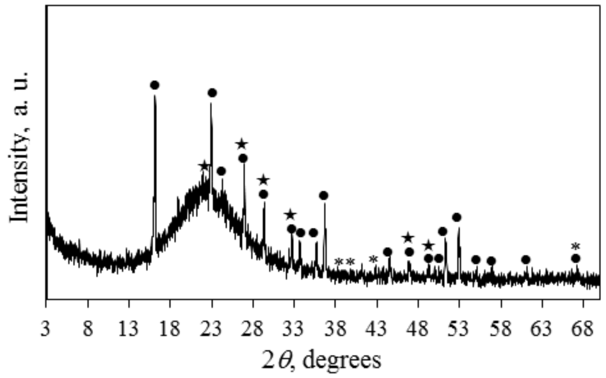


Fig. 2. X-ray diffraction pattern of silicagel dried at 50 °C for 48 h. Indexes: ● – $AlF_3 \cdot 3H_2O$; ∗ – Al_2O_3; ★ – $Fe_3(PO_4)_2 \cdot 3H_2O$

The pozzolanic activity was assessed using the modified method (Vektaris, B., et al [13]). This test consisted of placing the 1.000 g of mineral admixture and 500 ml of lime solution (1.200 g/l CaO). The solutions were kept for the first 48 h in a thermostat at 45 °C. At the end of the period, the 50 ml of solution was taken and the CaO content was determined for titration with 0.05 N hydrochloric acid (HCl) solution and using methylorange as indicator. The results were expressed by fixed CaO in milligrams per gram of pozzolanic additive. The remaining amount (450 ml of solution) was again kept for the 24 h at 45 °C. The process was repeated until the estimated value of the pozzolanic activity was insignificantly low (7 days).

The dilatometric analysis data was obtained by dilatometer Linseis L76. Heating rate of 2 ºC/min, the samples was heated up to 1070 ºC temperature under the ambient atmosphere.

Qualitative composition of raw materials was defined by the X-ray powder diffraction analysis (XRD). XRD data were collected with DRON-6 powder X-ray diffractometer with Bragg-Brentano geometry using Ni filtered CuK_α radiation, operating voltage 30 kV and emission current – 24 mA. The step-scan covered the angular range 2º – 70º (2θ) in steps of $2\theta = 0.02º$. X-ray fluorescence analysis (XRF) was performed by using S4 explorer with CuK_α radiation; the operating voltage was 20 kV and the emission current was 5 mA.

Scanning electron microscopy (SEM) (FEI Quanta 200 FEG) was performed using an accelerating voltage of 20 kV and a working distance of 10 mm for SEM observation.

Simultaneous thermal analysis (STA: differential scanning calorimetry – DSC and thermogravimetry – TG) was carried out on a Netzsch instrument STA 409 PC Luxx with ceramic sample handlers and crucibles of Pt-Rh. Heating rate of 15 ºC/min, the temperature ranged from 30 ºC up to 1000 ºC under the ambient atmosphere.

3. RESULTS AND DISCUSSION

3.1. Clay

Clays from industrial Dukstyna and Saltiskiai quarry were used in this investigation. According to XRD analysis data (Fig. 1), the kaolinite (*d*-spacing: 0.710, 0.441, 0.356, 0.249, 0.232 nm), feldspar (*d*-spacing: 0,416, 0.326, 0.322, 0.297 nm), illite (*d*-spacing: 1.000, 0.502, 0.334, 0.200 nm), muscovite (*d*-spacing: 0.997, 0.499, 0.333, 0.199 nm), chlorite (*d*-spacing: 1.412, 0.706, 0.470, 0.353 nm), hematite (*d*-spacing: 0.270, 0.251, 0.169 nm), quartz (*d*-spacing: 0.425, 0.334, 0.245, 0.181, 0.154 nm), dolomite (*d*-spacing: 0.288, 0.219, 0.178 nm) and calcite (*d*-spacing: 0.302, 0.228, 0.209, 0.189, 0.186 nm) were found in clays. It was determined [14] that 10.09 wt.% of mineral kaolinite, which might assume the active form at high temperature, is in Dukstyna clay. Meanwhile in clay of Saltiskiai quarry 2.95 wt.% of kaolinite was established. These clays are differing not only in kaolinite, but also in CaO quantities. According to the chemical composition of clays (Table 1), 10.19 wt.% and ~1 wt.% of CaO are in Saltiskiai and Dukstyna clays respectively.

In order to define the maximum calcination temperatures of clays, the dilatometric analysis was performed. Considering to dilatometric analysis data (Fig. 3), it was determined that in Saltiskiai clay the liquid phase onset is characterized by sudden changes in length of the sample at 730 °C, while in the Dukstyna clay sample the beginning of the process is fixed at higher ~860 °C temperature.

These data were confirmed by the STA analysis results. In the DSC curve of Saltiskiai clay (Fig. 4, a, curve 2) a significant endothermic peak observed at 650 °C – 780 °C temperature range was mainly due to decomposition of carbonates and formation of the liquid phase beginning. The endothermic effects at 96 °C and 517 °C temperatures are ascribed to removal of moisture and dehydroxylation of kaolinite [15, 16] processes respectively. It was determined that the total weight loss of the sample consists 13.52 wt.%. In the DSC curve of Dukstyna clay (Fig. 4, b, curve 2), excluding peaks characterizing the moisture removal (74 °C) and dehydroxylation of kaolinite (498 °C) processes, the endothermal effects at 303 °C and 576 °C temperatures were identified, which are characterized by modification of aluminum compounds and SiO_2 phase transition respectively. Contrary to analysis data of the above mentioned sample, in the 630 °C – 720 °C temperature range identified a broad endothermic effect is characterized by dolomite and calcite decomposition whereas the formation of a liquid phase is possible at higher than 860 °C temperature. It was found that Dukstyna clay sample lose 9.31 wt.% at 30 °C – 900 °C.

Thus, it can be stated that the maximum calcination temperature of Saltiskiai clay is 730 °C, while Dukstyna clay – 860 °C.

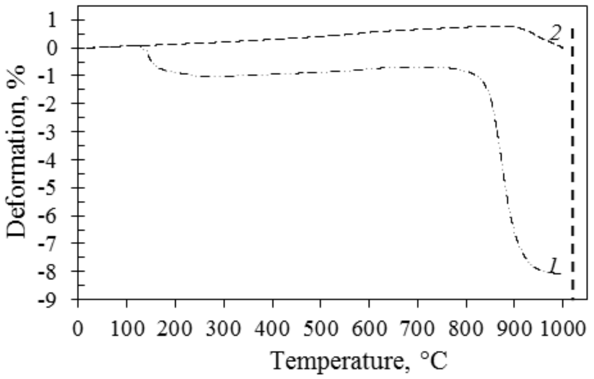
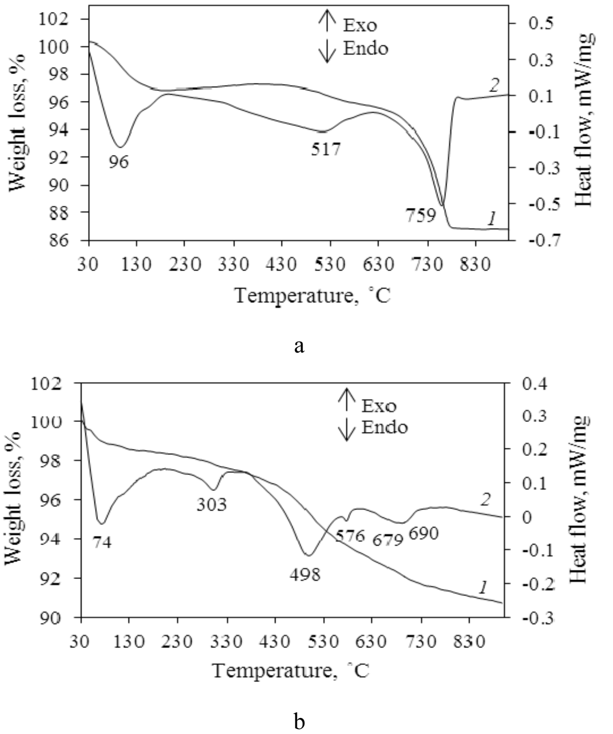


Fig. 3. Dilatometric analysis curves of clays from: 1 – Saltiskiai quarry; 2 – Dukstynos quarry

Considering the results obtained by dilatometric and STA analysis, the powder of Dukstyna clay was calcined at 600, 700, 800, 860 °C temperature for 1 h. It was determined that during thermal treatment at 600 °C the clay mineral kaolinite decomposes, because the main peaks of the mentioned compound disappears in the XRD curve (Fig. 5, curve 1). In addition, the diffraction peaks characteristic of potassium aluminum silicate $KAl_3Si_3O_{11}$ (*d*-spacing: 0.451, 0.336, 0.259, 0.201 nm) were identified. It should be noted that a type of the calcination products XRD curve, compared with XRD curve of raw Dukstyna clay (Fig. 1, curve 1), remains similar and the same clay minerals (except kaolinite) were identified. During the calcination at higher temperature (860 °C), the completely decarbonisation of dolomite and calcite, also the partially decomposition of muscovite and illite occurs, as a lower-intensity peaks of mentioned clay minerals were identified in the XRD curve (Fig. 5, curve 2). Besides, a very low-intensity diffraction peaks characteristic of periclase – MgO (*d*-spacing: 0.210, 0.148 nm) were identified.



a

b

Fig. 4. Simultaneous thermal analysis curves of clays from: a – Saltiskiai quarry; b – Dukstyna quarry; 1 – TG; 2 – DSC

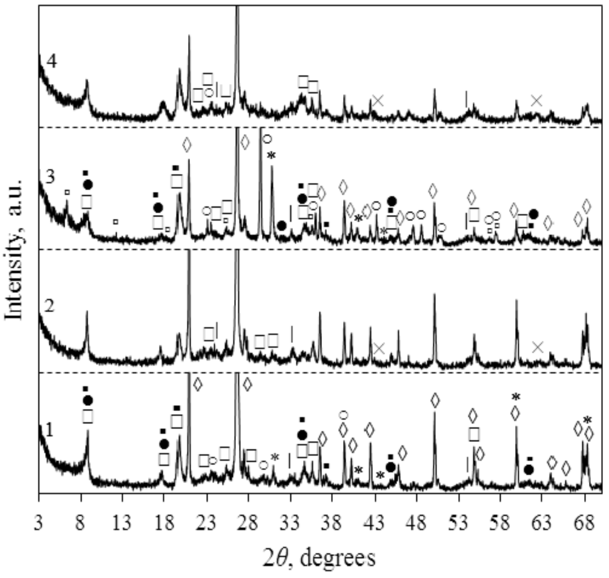


Fig. 5. X-ray diffraction pattern of calcined Dukstyna and Saltiskiai clays at different temperatures: 1 – D-600 °C; 2 – D-860 °C; 3 – Š-600 °C; 4 – Š-730 °C. Indexes: ● – illite; ▪ – muscovite; ◊ – quartz; ○ – calcite; * – dolomite; | – hematite; ▫ – chlorite; – potassium aluminum silicate; × – periclase

Clay of Saltiskiai quarry was calcined at 600, 700, 730 ºC temperature for 1h. In the XRD curve of the clay burned at 600 ºC (Fig. 5, curve 3) the diffraction peaks of kaolinite disappears. As in case of the thermal activated Dukstyna clay, the peaks characteristic of calcination product potassium aluminum silicate were identified. With increasing burning temperature (730 °C) carbonates are decomposed, the structure of chlorite is destroyed and the higher-intensity peaks of potassium aluminum silicate and low-intensity peaks of periclase were seen in the XRD curve (Fig. 5, curve 4).

In the next stage of the research the pozzolanic activity investigation was carried out. It was determined that the pozzolanic activity of Saltiskiai clay (600 ºC; 1 h) was 104 mgCaO/g (Fig. 6). It should be noted that the activated clay ability to bind CaO from the solution decreases with increasing burning temperature of the samples as the pozzolanic activity of calcined clay at 730 ºC temperature was almost 2 times lower (55 mgCaO/g). This might be caused by the formation of the inert phase such as periclase and integration of active SiO_2 into composition of other compounds. Meanwhile the pozzolanic activity value of the thermal activated Dukstyna clay (600 ºC; 1 h) was determined 1.5 times higher (157 mgCaO/g) (Fig. 7) than of the last mentioned clay sample. Presumably, the main reason of this is the major content (3.42 times) of kaolinite which assumed to its active form at 498 ºC temperature (Fig. 4, b). Although the pozzolanic activity of calcined Dukstyna clay at 700 °C was slightly altered to 154 mgCaO/g, but the same trend of pozzolanic activity, like on Saltiskiai clay samples, was observed – the pozzolanic activity of Dukstyna clay decreased (860 ºC; 134 mgCaO/g) when the samples were calcined at higher than 600 °C temperature.

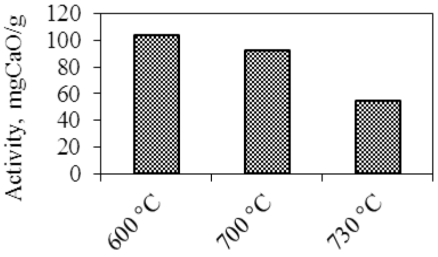


Fig. 6. The pozzolanic activity of calcined clay of Saltiskiai quarry

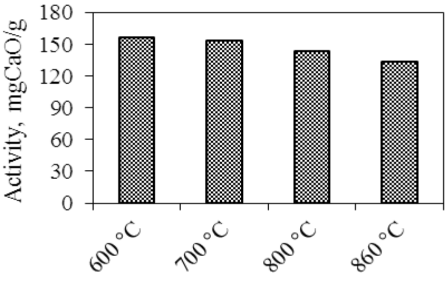


Fig. 7. The pozzolanic activity of calcined clay of Dukstyna quarry

It should be stated that at 600 ºC – 860 ºC temperature range calcined clays have a low pozzolanic activity (<180 mgCaO/g). In order to increase the pozzolanic activity the active SiO_2 should be used.

3.2. Silica gel

Silica gel – a waste of AlF_3 production – was used as a source of active SiO_2.

According to the XRD analysis data (Fig. 2) it was determined that the main impurity on dried silica gel was aluminum fluoride trihydrate ($AlF_3{\cdot}3H_2O$) (*d*-spacing: 0.545, 0.386, 0.329, 0.244 nm). Due to the dehydration of crystallization water from the $AlF_3{\cdot}3H_2O$ structure at 130 ºC – 230 °C, the samples lose 5.50 wt.% during this process (Fig. 8). At 694 °C temperature identified blurred endothermic effect is characterized by aluminum trifluoride phase transition. In addition the exothermal effect observed at 740 ºC – 950 ºC temperature range is associated with formation of a new phase in material. It was found, that silica gel sample loses 9.51 weight percentages in temperature range from 30 ºC to 1000 ºC.

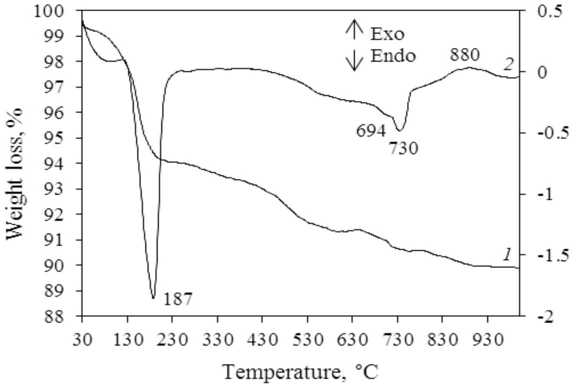


Fig. 8. Simultaneous thermal analysis curves of dried silica gel: 1 – TGA; 2 – DSC

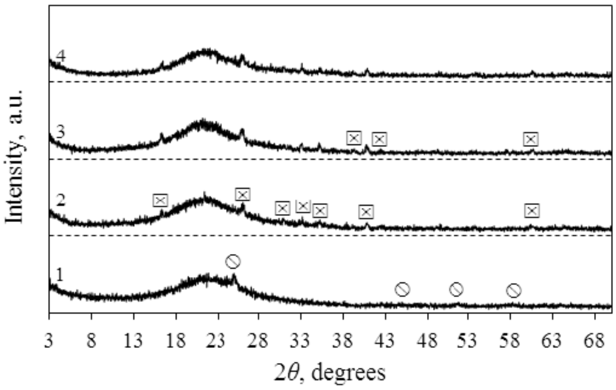


Fig. 9. X-ray diffraction pattern of thermal treated silica gel at different temperatures: 1 – 600 ºC for 1 h; 2 – 700 ºC for 1 h; 3 –800 ºC for 1 h; 4 – 900 ºC for 1 h. Indexes: ☒ – mullite ($Al_{4.95}Si_{1.05}O_{9.52}$); ⦸ – aluminum fluoride (AlF_3)

Considering to the STA analysis data (Fig. 8) a silica gel was calcined at 600, 700, 800, 900 ºC temperature for 1 h. It was established that during thermal treatment at 600 ºC the anhydrous aluminum fluoride (AlF_3) was composed as the main peaks (*d*-spacing: 0.352, 0.219, 0.176, 0.158 nm) characteristic to this compound were identified in the XRD curve (Fig. 9, curve 1). It can be stated that the structure of AlF_3 is unstable at the higher temperature (700 ºC – 900 ºC), because the main peak (*d*-spacing: 0.352 nm) of the mentioned compound disappears in the XRD curves (Fig. 9, curves 2 – 4). Furthermore, in fired product the diffraction peaks characteristic of mullite (*d*-spacing: 0.540, 0,342, 0,340, 0,220 nm), which intensities increased when the burning temperature was raised, in the XRD curves of calcined silica gel at 700 ºC and higher temperature were identified. This data coincident with results obtained by other researchers [17] and indicate that the formation of mullite in the systems, containing's fluorine ions occurs at conditional low temperatures.

In order to estimate the influence of temperature on evaporation of fluoride ions, the XRF analysis of silica gel fired products was carried out (Fig. 10). It was measured that 8.14 wt.% of F^- ions was in silica gel after burning at 600 ºC for 1h, i. e. content of F^- ions was 5.78 % lower compared to the obtained results on the dried silica gel (Table 1). Meanwhile, the content of F^- ions reduced ~42 % in material after thermal treatment at 700 ºC. When the calcination temperature was raised to 800 ºC and 900 ºC, respectively 0.83 wt.% and 0.31 wt.% of F^- ions remained in silica gel. Thus, it can be stated that at higher than 600 ºC temperature, the content of F^- ions on silica gel is reduced and according to XRD analysis results (Fig. 10), during calcination process the fluorine ions are not combined to another compounds but directly passed to atmosphere.

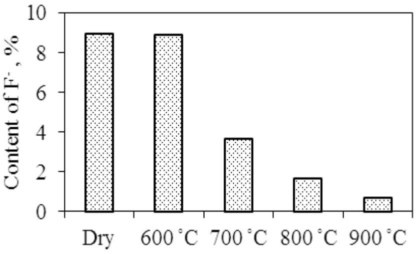


Fig. 10. Content of F^- ions (%) on silica gel after thermal treatment at different temperatures

The structure changes of crystals after silica gel calcination at 600 ºC – 900 ºC was observed on SEM micrographs (Fig. 11, a – e). As shown in the Fig. 11, tetragonal modification crystals of $AlF_3\cdot3H_2O$ ((2.5 – 3) μm×(4 – 8) μm) lose their typical form during burning at high temperature. In addition, at 700, 800, 900 ºC burned silica gel micrographs (Fig. 11, c – e) a fine fiber crystals were identified. The formation of these crystals confirmed the results of STA (Fig. 8) and XRD (Fig. 9, curves 2 – 4) analyses and suggested the formation of mullite.

After silica gel pozzolanic activity investigation it was determined that the ability to combine the CaO from the solution reduced when the calcination of silica gel at higher temperatures was carried out. Following the 3 days interaction of silica gel with $Ca(OH)_2$, the highest initial pozzolanic activity (164 mgCaO/g) (Fig. 12) of the burned sample at 700 ºC was measured. The activity of this sample remains a major up to 6 days (248 mgCaO/g). Meanwhile, the pozzolanic activity of the silica gel sample burned at 600 ºC (265 mgCaO/g), there in fired product a mullite nucleations were not formed, increased above the last-mentioned sample pozzolanic activity (258 mgCaO/g). It was observed that burned silica gel samples (800, 900 ºC), due to inactive glass phase of mullite, had the same pozzolanic activity throughout the investigation.

Thus, according to the research results, it can be stated that after 7 days interaction of silica gel with $Ca(OH)_2$, at 600 ºC burned sample exhibited the highest pozzolanic activity (265 mgCaO/g) whereas at 800 ºC and 900 ºC temperature fired silica gel had the lowest – 192 mgCaO/g (Fig. 12).

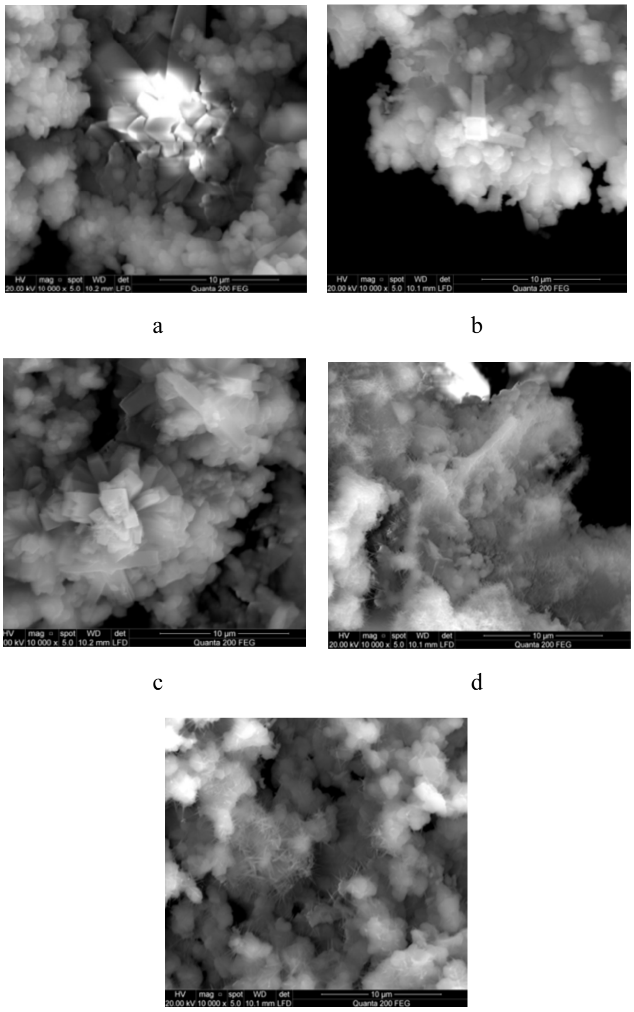

a b
c d
e

Fig. 11. Scanning electron microscopy micrographs of silica gel after thermal treatment at different temperatures for 1 h: a – dried silica gel; b – 600 ºC; c – 700 ºC; d – 800 ºC; e – 900 ºC

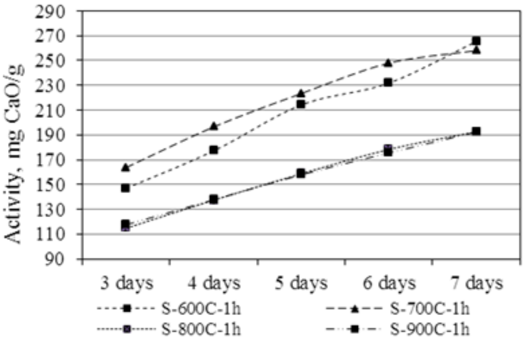


Fig. 12. The diagram of calcined silica gel pozzolanic activity range during 7 days

3.3. Clay-silica gel composites

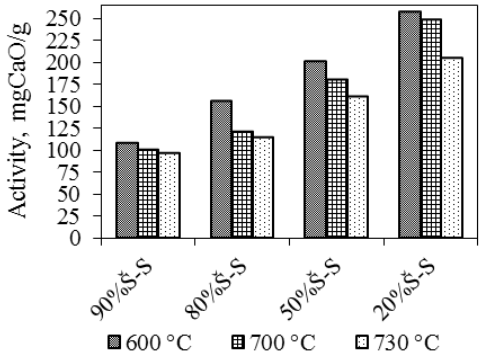
According to the results of pozzolanic activity investigation, in this stage of research the influence of silica gel to pozzolanic activity of calcined clays-silica gel composites was explored.

As expected, a pozzolanic activity of the samples was improved when the additive of active SiO_2 was added into the clay-silica gel mixtures. It was established that after 7 days the pozzolanic activity of calcined Saltiskiai clay with 10 wt.% silica gel additive (600 ºC; 1 h) was 109 mgCaO/g (Fig. 13), i. e. 5 % higher than pozzolanic activity of pure calcined Saltiskiai clay sample (104 mg CaO/g, Fig. 6). It was also found that the ability to combine the CaO from solution of composites grew when the major amount of additive was used. It was noted that the pozzolanic activity increased about 2 times when 50 wt.% silica gel was added into composite (201 mgCaO/g) and with 80 wt.% additive the pozzolanic activity of composite reach 257 mgCaO/g. The same tendency of decreasing pozzolanic activity with increasing temperature of calcination in the system of Saltiskiai clay-silica gel as in the burned Saltiskiai clay sample was estimated. Despite this fact, the pozzolanic activity with 10 wt.% additive (97 mgCaO/g) (Fig. 13) became 1.8 times higher than with pure calcined clay sample (54 mgCaO/g) (Fig. 6).

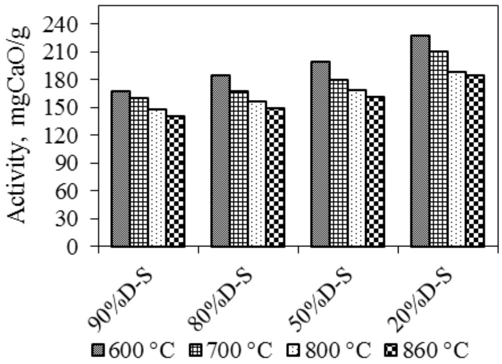
The results of pozzolanic activity investigation of calcined Dukstyna clay-silica gel composites, there amount of silica gel additive varied from 10 wt.% to 80 wt.%, shown (Fig. 14) that the silica gel additive positively effected on Dukstyna clay-silica gel composites pozzolanic activity as in the case of last-mentioned composites (Fig. 13). It was determined that the pozzolanic activity of fired composite with 10 wt.% of silica gel additive (600 ºC; 1 h) was ~7 % higher (168 mgCaO/g) (Fig. 14) than pozzolanic activity of pure calcined Dukstyna clay sample (157 mg CaO/g, Fig. 7). Thus, the pozzolanic activity of the composites increased with increasing content of silica gel additive in the system. However, independently of the additive amount, the pozzolanic activity of composites reduced when the burning at higher than 600 ºC temperature was carried out. Hence, when the Dukstyna clay-silica gel composites were calcined at 860 ºC temperature, the pozzolanic activity value approximately 1.3 times reduced.

According to the obtained results it can be stated that the Saltiskiai clay-silica gel and Dukstyna clay-silica gel composites, which were fired at 600 ºC, exhibited the best properties of activity. This may be caused by a few factors: dehydroxylation of clay mineral kaolinite and transition to active amorphous phase of metakaolinite; increased content of the active amorphous phase with addition of silica gel; 600 ºC temperature was too low to formation of inert compounds or their nucleation's as at 700 ºC inactive phase of mullite was composed (Fig. 9). These propositions were confirmed by the XRD analysis data of the calcined clays-silica gel composites (Figs. 15, 16).

After calcination of Saltiskiai clay with 10 wt.% silica gel additive at 600 ºC temperature, in the fired product XRD curve (Fig. 15, curve 1) the same compounds, as in the calcined clay XRD curve (Fig. 5, curve 3) were identified, i. e. unidentified a new compounds of crystalline or semi-crystalline structure, which could positively react with CaO when investigation of pozzolanic activity was



13 pav. The pozzolanic activity of calcined Saliskiai clay-silica gel composites



14 pav. The pozzolanic activity of calcined Dukstyna clay-silica gel composites

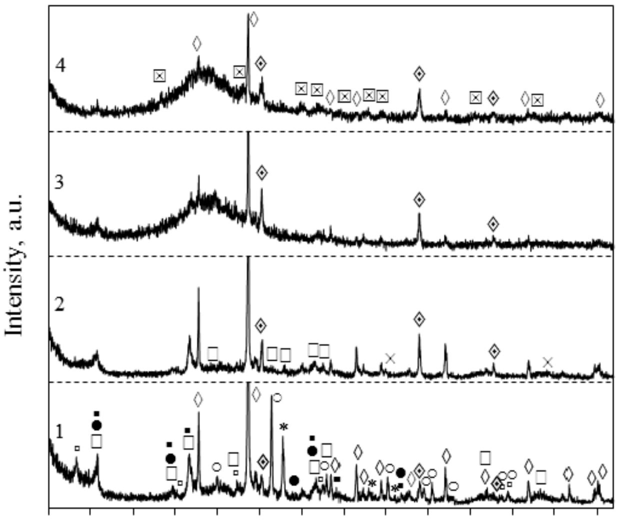


Fig. 15. X-ray diffraction pattern of calcined Saltiskiai clay-silica gel composites at different temperatures: 1 – 90 %Š-10 %S-600 ºC; 2 – 90 %Š-10 %S-730 ºC; 3 – 20 %Š-80S-600 ºC; 4 – 20 %Š-80S-730 ºC. Indexes: ● – illite; ▪ – muscovite; ◊ – quartz; ○ – calcite; * – dolomite; ▫ – chlorite; – potassium aluminum silicate; ◈ – fluorite; × – periclase; ☒ – mullite

carried out. Contrary to this, the diffraction peaks characteristic of CaF_2 (*d*-spacing: 0.315, 0.193, 0.164 nm), which composed due to the reaction of fluorine and calcite, were identified in the XRD curve. The intensity of mentioned compound diffraction peaks slightly increased, meanwhile the diffraction peaks of calcite and dolomite almost disappears after burning at 730 ºC temperature (Fig. 15, curve 2). In the XRD curve of burned composite with 80 wt.% of silica gel (600 ºC) (Fig. 15, curve 3) the intensive diffraction peaks of CaF_2 and one of the main diffraction peak of illite (*d*-spacing: 1.000 nm) and muscovite (*d*-spacing: 0.997 nm) were identified (other peaks were covered with a broad peak in the angle of diffraction that varied from 20º to 24º, which defined the existence of amorphous phase in the system and caused a great pozzolanic activity of the clay-silica gel composites). Moreover, during the calcination at higher temperature (730 ºC) the mullite was formed (Fig. 15, curve 4), which had a negative influence on pozzolanic activity of calcined Saltiskiai clay with 80 wt.% of silica gel composites.

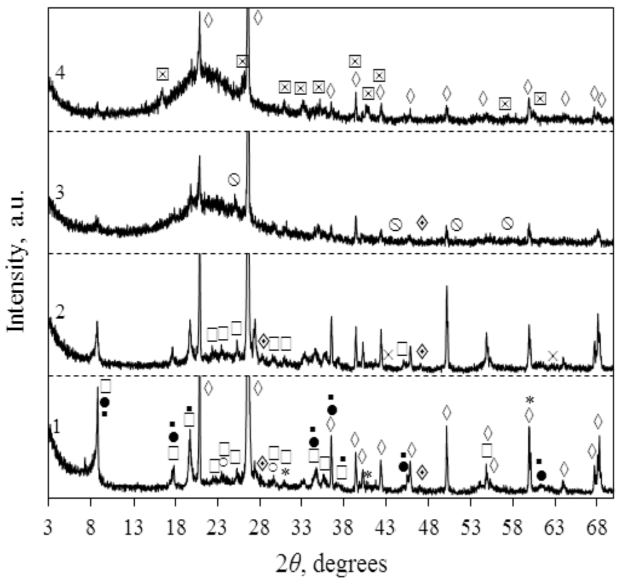


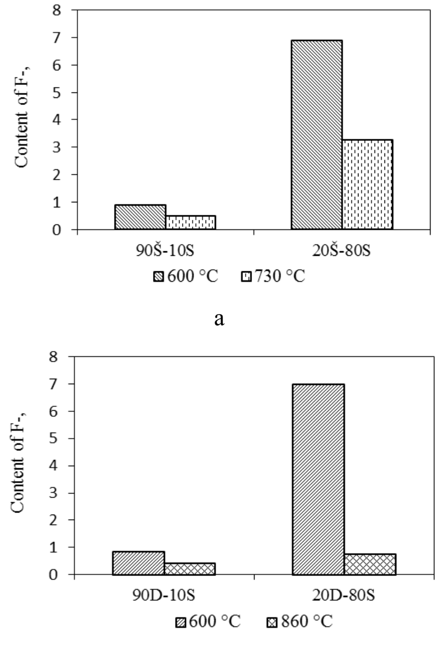
Fig. 16. X-ray diffraction pattern of calcined Dukstyna clay-silica gel composites at different temperatures: 1 – 90 %D-10 %S-600 ºC; 2 – 90 %D-10 %S-860 ºC; 3 – 20 %D-80 %S-600 ºC; 4 – 20 %D-80 %S-860 ºC. Indexes: ● – illite; ▪ – muscovite; ◊ – quartz; ○ – calcite; * – dolomite; ▫ – chlorite; – potassium aluminum silicate; ◈ – fluorite; × – periclase; ☒ – mullite; ⦸ – aluminum fluoride

It was determined that in the XRD curve of Dukstyna clay-silica gel composite containing 10 wt.% of silica gel and burned at 600 ºC, without a very low-intensity diffraction peaks of CaF_2, the same calcination products formed during thermal treatment of Dukstyna clay sample (Fig. 5, curve 1) were identified. After burning of the composites at 860 ºC temperature, the intensity of diffraction peaks characteristic of potassium aluminum silicate were increased, while intensity of illite and muscovite diffraction peaks became lower, i. e. a partial destruction of crystalline lattice took place (Fig. 16, curve 2). Furthermore, in the XRD curve of composite with 80 wt.% of silica gel and burned at 600 ºC (Fig. 16, curve 3), without diffraction peaks of last-mentioned compounds and contrary to calcination products of Saltiskiai clay-silica gel, diffraction peaks of $AlF_3 \cdot 3H_2O$ dehydration product AlF_3 were identified. It should be noted that during thermal treatment of composites at 860 ºC in the Dukstyna clay-silica gel system the mullite was formed as the diffraction peaks of mentioned compound were identified in the XRD curve (Fig. 16, curve 4).

In the calcination products of clay-silica gel composites the content of F^- ions was determined by the XRF analysis and presented on Fig. 17. As shown, 0.89 % of F^- ions were estimated on the Saltiskiai clay-silica gel composite with 10 wt.% silica gel additive and calcined at 600 ºC temperature (Fig. 17, a). Meanwhile, the content of F^- ions reduced to 0.5 % in composite burned at 730 ºC temperature. In addition, when 80 wt.% of silica gel was added to the Saltiskiai clay-silica gel system, the F^- ion content in composite fired at 730 ºC, was decreased in half compared to content of F^- ions determined at 600 ºC burned composite (6.91 %).

It was determined that 0.42 % of F^- ions remained on the Dukstyna clay-silica gel composite with 10 wt.% of silica gel after thermal treatment at 860 ºC (Fig. 17, b). Meanwhile, when 80 % of additive was used and composites were fired at 600 ºC and 860 ºC temperature, the 6.99 % and 0.76 % of F^- ions were established respectively.

Thus, it can be stated that due to lack content of CaO in the clay-silica gel system, not all F^- ions were combined to CaF_2 and at the higher than 600 ºC temperature the rest of F^- ions were released into atmosphere.



a

b

Fig. 17. Diagrams of F^- content on calcined clays-silica gel composites: a – Saltiskiai clay-silica gel; b – Dukstyna clay-silica gel

4. CONCLUSIONS

- It was found that clays of Dukstyna and Saltiskiai quarry have insufficient pozzolanic properties. The highest pozzolanic activity (157 and 104 mgCaO/g) of Dukstyna and Saltiskiai samples is reached after thermal treatment at 600 ºC for 1 h.

- The pozzolanic activity of burned clay samples decrease with increasing calcination temperature from 700 ºC to 860 ºC.
- It was determined that the silica gel has a good pozzolanic activity (265 mgCaO/g) after thermal treatment at 600 ºC for 1 h. At 700 ºC – 900 ºC temperature range, concerning to the mullite phase, the pozzolanic activity of silica gel decreases, but remains higher than 190 mgCaO/g.
- It was found that the fired clay-silica gel composites have a higher pozzolanic activity than a pure calcined clay samples. When the 10 wt.% of silica gel additive is used, the pozzolanic activity of Saltiskiai clay-silica gel and Dukstyna clay-silica gel composites increases respectively 5 % and 7 %, while addition of 80 wt.% of silica gel, increase the pozzolanic activity to 257 and 229 mgCaO/g respectively after thermal treatment at 600 ºC for 1 h. However, independently of the additive amount, the pozzolanic activity of composites decreases when the calcination at higher than 600 ºC temperature is carried out.

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