ANHYDRITE BINDER CALCINED FROM PHOSPHOGYPSUM

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The phosphogypsum – dihydrate calcium sulphate is waste material of phosphoric acid production from the Kola apatites. The possibility of applying lime neutralized phosphogypsum as a raw material for obtaining anhydrite binder was investigated in this paper. The effect of the calcination temperature and of following additives: dust from a cupola furnace, ground glass and clay on the properties of obtained product was studied. The products were characterized by X–ray diffraction analysis, simultaneous thermal analysis, Fourier-transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) analysis. It was determined that the phosphogypsum with additives calcined at the temperature 900 ºC, and the following grinding of it to the specific surface area 600 ± 10 m^2/kg allow obtaining the fast setting anhydrite binder. The anhydrite binder calcined with the addition of 5% ground glass exposes the best physical and mechanical properties: the setting duration up to 13-38 min, the compressive strength of the dry samples is 30.74 MPa.

INTRODUCTION

Anhydrite cement is largely applied in the construction industry in many countries. The anhydrite cement is calcined gypsum at the high temperature (600-700°C) and it is ground with activators [1]. The large underground layers of natural anhydrite are lying in Lithuania, but they are at the depth of 150-300 m and they are not quarried in practice [2].

The suitable sulphate raw material for production of gypsum and anhydrite binding materials is phosphogypsum - a phosphoric acid production waste, comprising up to 92-95 % of $CaSO_4 \cdot 2H_2O$. In Lithuania, SC Lifosa produces near 430 thousands tons of the phosphoric acid and 4-5 times more of phosphogypsum per year, which is usually dumped in large stockpiles and causes serious environmental damage [3]. The use of it would be useful in the manufacture of building materials economically and ecologically.

The only 15 % of phosphogypsum is used in the manufacture of binding materials worldwide [4]. The application of phosphogypsum in production of binding materials is burdened by the presence of phosphate, fluoride and other soluble impurities. Nevertheless, the phosphogypsum is successfully applied for the production of anhydrite cement in some countries [5-7]. Basically, the methods of neutralizing the impurities of phosphogypsum and of the additional treatment (washing, thermal or chemical extraction) before calcinations differ only.

The scientists of Lithuania have created the progressive technology for neutralizing acid unwashed phosphogypsum, which enables effectively the use of this material in the manufacture of binding materials [8, 9]. A possibility to use an unwashed, waste phosphogypsum neutralized by lime-dihydrate calcium sulphate in order to obtain an anhydrite binding material was determined in [6].

Different authors have suggested different temperatures for the preparation of anhydrite binding material. The manufacture of anhydrite cement from phosphogypsum is recommended by Indian scientists Sing M. and Garg M. [5]. Data showed that a stable anhydrite can be produced by heating phosphogypsum at the temperature 1000°C. When phosphogypsum heated at elevated temperature produced an anhydrite, phosphate and fluoride impurities became inert. The strongest samples were obtained with the use of sodium sulphate and ferrous sulphate activators together. The same authors [10] pointed out that phosphogypsum, which was calcined at the temperature 900-1000°C to anhydrite and was mixed with suitable chemical activators, achieved a high strength and it was recommended for manufacture of flooring tiles.

The activation of anhydrite cement can be increased by grinding it with additives [1, 5, 10] or by dissolving the activators in the water during the formation process of samples [6, 7, 11, 12]. The influence of the following setting activators: Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $FeSO_4$,

$CaCl_2$, $K_2Cr_2O_7$ was investigated in several studies [5, 6, 7, 11, 12, 13, 14].

The scientists [15] have created the mixture of raw materials, which calcined at 900-950 ℃, produced fast setting anhydrite binding material of high quality: the compressive strength of dry samples after 28 days was 51.2-72.1 MPa. The main component was the neutralized phosphogypsum and the following additives: clay and calcium including neutralized glass pulp or a neutralized pulp of silicofluoric acid (waste of fertilizers production).

Kazragis et al. [16] investigated the possibilities of high temperature producing binders at gypsum or phosphogypsum and kaolin. Included in the composition of kaolinite the oxides of Al_2O_3 and SiO_2 can be with CaO of gypsum at high temperature form the silicates and aluminates as well as the aluminosilicates of calcium. The thermodynamical calculations show that, in this case (500-1200 ℃), the compounds C_3S, C_3A a.o. can be formed, which are in the composition of Portland cement. The calcium silicates, aluminates and aluminosilicates (for example: C_2S, C_3S, C_3A, AS_2 a.o.) can be formed between gypsum or phosphogypsum and kaolin at high temperature. The X-ray diffraction techniques confirmed the existence of C_3S, A_3S_2, CAS_2, C_2AS in the binders using gypsum or phosphogypsum and kaolin.

The aim of this work is to investigate the possibility of obtaining the fast setting anhydrite cement from neutralized phosphogypsum, which would expose the high-quality properties of binding and of strength.

EXPERIMENTAL

The phosphogypsum - dihydrate calcium sulphate, waste material of phosphoric acid production (from the Kola apatites) was the main material for the investigation. It was taken from the stockpiles of ortho-phosphoric acid production waste at Stock Company (SC) Lifosa. Dihydrate phosphogypsum was neutralized in lime suspension (water/lime ratio - 0.004) according to methodology [8, 9] to pulp pH 11.0-11.5 of phosphogypsum with ratio of water and gypsum (W/G = 1). The neutralized phosphogypsum has been filtrated and dried at the temperature 100 ± 2°C.

The pure CaO was used for the neutralization of phosphogypsum (free CaO = 96 %, specific surface area 320 m^2/kg, Reachim, Russia).

The following activators: dust from a cupola furnace, ground glass and clay were used for calcining anhydrite binder. The dust from a cupola furnace is formed as the waste of production of glass wool at SC Paroc (Lithuania). The ground glass was obtained by grinding the breakage of green glass in porcelain ball mill (230 m^2/kg). The clay was brought from quarry at Kruna (Lithuania).

The mixtures of appropriate composition were prepared from the neutralized phosphogypsum, the dust from a cupola furnace, the ground glass and the clay (Table 1). The compounds were calcined at the temperatures 800°C and 900°C for 30 min in the muffle furnace.

Chemical composition of materials was determined by classical methods of chemical analysis according to the standards LST EN 196-2, GOST 20851.

The pH measurements of water suspension were conducted by pH-meter 673 M, when the ratio of water (W) and solid material (S) W/S = 10.

The hydration water (loss on ignition, %) in phosphogypsum was calculated after heating the material at the temperature 400 °C.

Materials were ground in a ball mill. The specific surface area was determined by the Blane's method according to EN 196-6.

The X-ray powder diffraction data were collected with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered CuKα radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2–70° (2θ) in steps of 2θ = 0.02°.

Simultaneous thermal analysis (STA: differential scanning calorimetry - DSC - and thermogravimetry - TG) was carried out on a Netzsch instrument STA 409 PC using a heating rate of 15°C/min. The temperature ranged from 30°C up to 1000°C under an air atmosphere. The ceramic sample handlers and crucibles of Pt–Rh were used.

FT-IR spectra have been carried out with the help of a Perkin Elmer FT-IR system Spectrum GX. Specimens were prepared by mixing 1 mg of the sample with 200 mg of KBr. The spectral analysis was performed in the range of 4000-200 cm^{-1} with spectral resolution of 1 cm^{-1}.

The microscopic analysis was conducted with scanning electron microscope FEI QUANTA 200F.

In order to estimate the compressive strength of anhydrite binder, cubes 2×2×2 cm size samples were formed up. The water rate and the setting time of formed mixture (normal consistence) were determined according to standard EN 196-3. The samples were hardened in 90 % relative humidity environment and compressed by press ELE Automat.

Table 1. Composition of calcined mixtures.

| Mixture No | Content of components (%) | | | |
	Phospho-gypsum	Dust from a cupola furnace	Ground glass	Clay
1	100	-	-	-
2	95	5	-	-
3	95	-	5	-
4	90	-	5	5
5	85	-	5	10

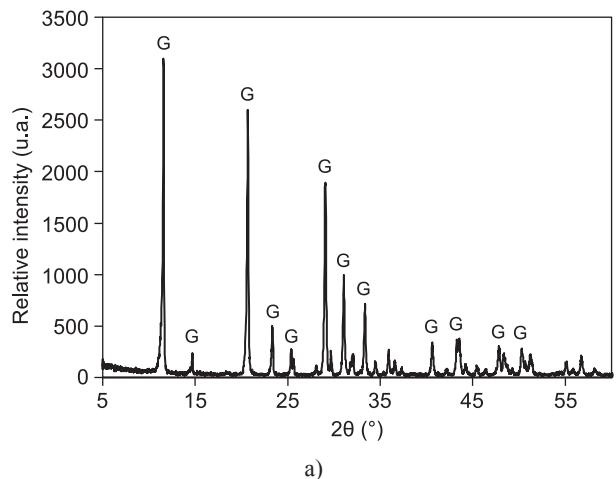## RESULTS AND DISCUSSION

The chemical composition of used materials

The chemical composition of phosphogypsum on average was the following (%): CaO - 31.90; SO_3 - 46.00; R_2O_3 - 1.02; P_2O_5 total - 0.60; including P_2O_5 water soluble - 0.10; F - 0.14; others - 0.40; loss on ignition - 19.69;
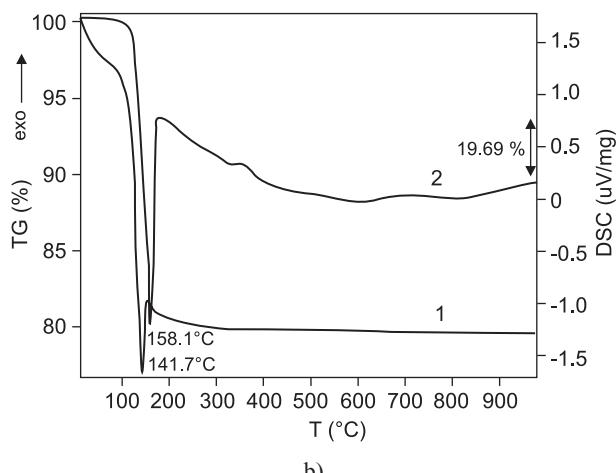
insoluble in HCl - 0.25. pH of the water suspension of raw phosphogypsum was 4.7-4.8, meanwhile pH of the phosphogypsum neutralized by lime (according to the method [9, 10]) was 11.0-11.5. The specific surface area was 392 m^2/ kg. X-ray diffraction pattern (Figure 1a) and STA curves (Figure 1b) of phosphogypsum showed that the dihydrate calcium sulphate $CaSO_4 \times 2H_2O$ prevailed in this compound.

The FT-IR spectrum of the neutralized and dried phosphogypsum is presented in Figure 1c. The spectrum contains absorption bands in the range 3600-3200 cm^{-1} and in the range 1680-1620 cm^{-1}, which are the characteristic of $CaSO_4 \cdot 2H_2O$ [17, 18]. These results are in accordance with the X-ray diffraction pattern in Figure 1a and STA curve in Figure 1b.
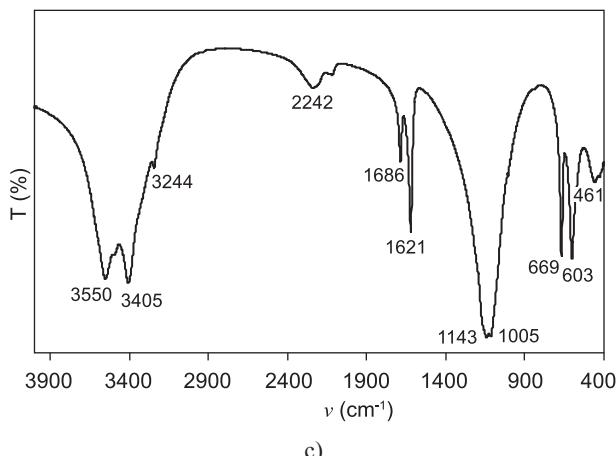
The chemical composition of the dust from a cupola furnace on average was the following (%): SiO_2 - 39.91; CaO - 3.57; MgO - 12.79; R_2O_3 - 19.24; Na_2O - 7.22; K_2O - 5.49; loss of ignition - 11.78. pH of water suspension

a)
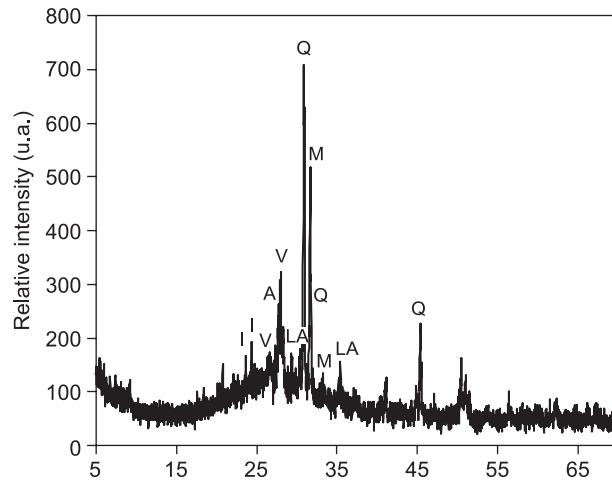

b)

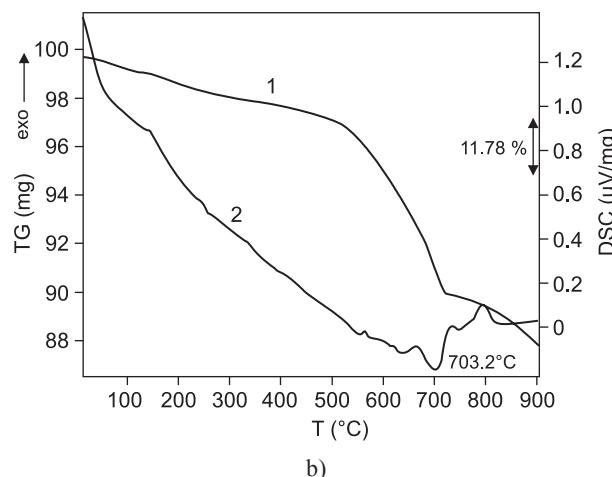
c)

Figure 1. X-ray diffraction pattern (a), STA curve (DSC - 1, TG - 2) (b) and FT-IR spectrum (c) of the phosphogypsum (G - $CaSO_4 \cdot 2H_2O$).

a)

b)

Figure 2. X-ray diffraction pattern (a) and STA curve (DSC - 1, TG - 2) (b) of the dust from a cupola furnace (Q - SiO_2 cristabolite, L - lisetite, V - vaterite, A - anorthite, M - magnesite, I - illite).
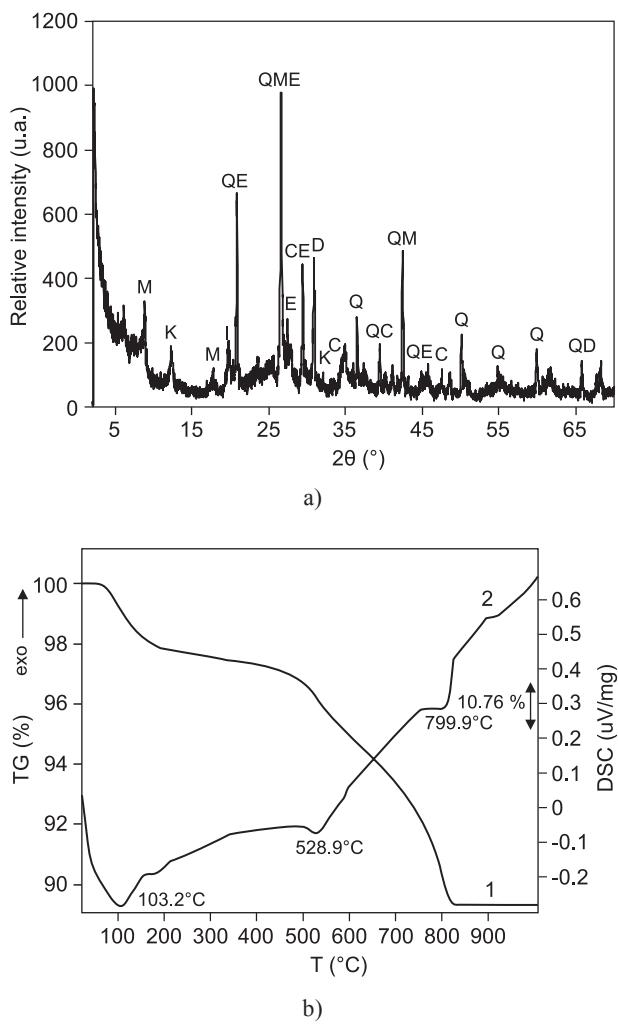
a)

b)

Figure 3. X-ray diffraction pattern (a) and STA curves (DSC - 1, TG - 2) (b) of the clay. (M - muscovite, K - kaolinite, I - ilite, C - calcite, E - microcline, Q - quartz, D - dolomite).

was 9.1-9.2. The specific surface area was 1900 m^2/kg. The cristabolite, the lisetite, the vaterite, the anorthite, the magnesite, the illite were identified in the X-ray diffraction pattern (Figure 2a). That was confirmed by the thermal analysis as well. The lisetite and the illite dehydrated in the temperature range 500-650°C (Figure 2b). The vaterite and the magnesite dissociated in the temperature range 650-800°C.

The chemical composition of the ground glass on average was the following (%): SiO_2 - 71.07; Na_2O - 13.69; K_2O - 1.08; Al_2O_3 - 1.75; CaO - 7.50; Fe_2O_3 - 0.39; MgO - 4.12; Cr_2O_3 - 0.2; SO_3 - 0.2. pH of its water suspension was 10.2 - 10.3. The specific surface area was 230 m^2/kg.

The chemical composition of the clay on average was the following, %: SiO_2 - 56.95; Al_2O_3 - 15.11; Fe_2O_3 - 5.50; CaO - 5.00; MgO - 4.30; Na_2O - 1.34; K_2O - 0.70; others - 0.34; loss on ignition - 10.76. pH of its water suspension was 8.2-8.3. The specific surface area was 267 m^2/ kg. The following minerals of the clay: the muscovite, the illite, the microcline, the kaolinite, as well as the quartz, the calcite, the dolomite were identified in the X-ray diffraction pattern (Figure 3a). The obtained results were confirmed by STA curve (Figure 3b). Using the outcome of thermal analysis, we see that the minerals of the clay dehydrated in the temperature range 450-650°C, meanwhile the calcite and the dolomite dissociated in the temperature range 650-900°C.

The properties of anhydrite binder

The X-ray diffraction analysis of anhydrite binder calcined at the temperatures 800 and 900 ºC allowed concluding that anhydrous calcium sulphate $CaSO_4$ - anhydrite prevailed in all the products (like the X-ray
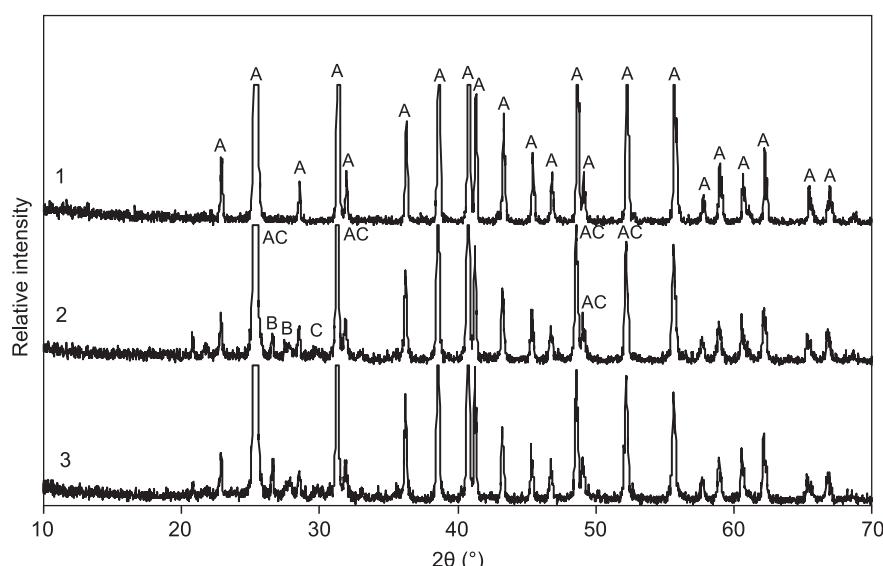

Figure 4. X-ray diffraction patterns of anhydrite binder calcined at 900 ºC: 1 - 1, 2, 3 mixtures, 2-4 mixture, 3-5 mixture; composition of mixtures is reported in Table 1 (A - anhydrite $CaSO_4$; B - anorthite $CaAl_2Si_2O_8$–CAS_2; C - gehlenite $Ca_2Al_2SiO_7$–C_2AS).

diffraction pattern 1, presented in Figure 4). In the X-ray diffraction patterns (Fig. 4 diffraction patterns 2, 3) of the products with additives of the ground glass and of the clay calcined at the temperature 900 ºC, the low amount of the following aluminosilicate of calcium: the anorthite $CaAl_2Si_2O_8$–CAS_2 and gehlenite $Ca_2Al_2SiO_7$–C_2AS was found additionally to the main component - calcium sulphate $CaSO_4$.

The FT-IR spectrums of the anhydrite binder calcined at 800 and 900°C (with additives as well is without additives) are alike (Figure 5). They do not include the absorption bands characteristic of crystal water of $CaSO_4$ $2H_2O$ (at 3550, 3405, 1686 and 1621 cm^{-1} see in Figure 1c) but include the absorption bands characteristic of insoluble anhydrite (at 675, 614, 595 cm^{-1}) only [19, 20].

The neutralized phosphogypsum calcined without the additives at the temperatures 800 and 900°C exhibited the properties of binding (Table 2), but the setting duration of it was very long. At the temperature 800°C, the obtained unground material started to bind after 240 h and terminated after 246 h (specific surface area - 350 m^2/kg). At the higher temperature - 900°C,

Figure 5. FT-IR spectrum of the anhydrite binder calcined at 800 and 900ºC.

the obtained unground anhydrite binder (specific surface area - 300 m^2/kg) started to bind earlier: initial time of binding - 144 h, final time - 168 h.

The binding and hardening of the anhydrite binder became faster after grinding it to the specific surface area 600 ± 10 m^2/kg. At the temperature 800°C, the obtained material started to bind after 8 h 30 min and terminated after 9 h 30 min. At the higher temperature (900°C), the initial time of the binding shortened to 5 h 45 min, and the final time - to 8 h 20 min.

In order to explain the effect of the calcination temperature on the properties of the anhydrite binder the studies of the microstructure of the material were carried out.

We see (Figures 6, 7) that the prismatic and rhombic (tabular) shape crystals of irregular boundaries and stackings are formed. The crystals of the anhydrite calcined at the temperature 800°C are small-size particles and they are arranged irregularly (Figure 6). Their surface is crannied (Figure 6c). It is possible to predict that the evaporation of the crystallization water evoked the formation of the microcracks in the crystal structure of the investigated material. Meanwhile, the surface of the crystals calcined at the temperature 900°C (Figure 7) is smoother and melted - without microcracks. These crystals are larger and they form hard agglomerated aggregates. The tabular microcrystal aggregates prevail. The agglomeration is characterized by the increase of the contact area among the particles [19]. The grinding of the calcined anhydrite binder (with additives as well as without additives) to the same specific surface area (600 ± 10 m^2/kg) at the different temperatures proved the proposition that the calcined material at the temperature 900°C is harder, because the grinding duration is almost 4 times (from 25-30 till 110-115 min) longer in comparison with the material obtained at the temperature 800°C.

The properties of ground and unground anhydrite binder at the different temperatures can be explained
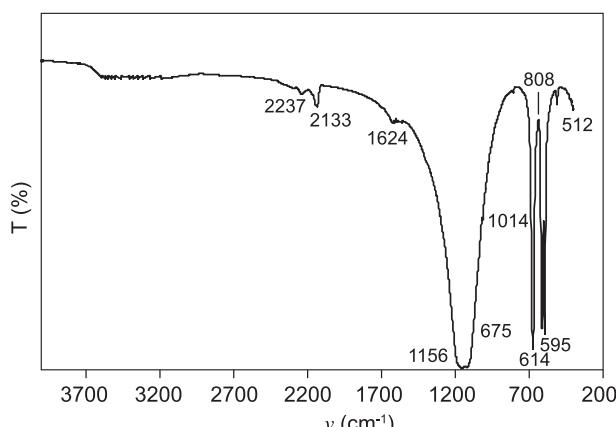
Table 2. Characteristic properties of the anhydrite binder produced from phosphogypsum.

Mixture No	Temperature of calcination (ºC)	Specific surface area (m^2/kg)	W/A	Setting time (h/min)	
				Initial	Final
1*	800	350	0.55	240/00	246/00
1	800	600	0.34	8/30	9/30
2	800	600	0.34	2/06	2/31
3	800	600	0.34	0/35	1/00
4	800	600	0.34	5/20	6/15
5	800	600	0.34	4/06	7/29
1*	900	300	0.37	144/00	168/00
1	900	600	0.29	5/45	8/20
2	900	595	0.29	0/40	0/52
3	900	600	0.29	0/13	0/38
4	900	590	0.29	0/26	0/42
5	900	595	0.29	0/52	1/10

* unground anhydrite binder; W/A - water/anhydrite binder

by the differences in the crystal structure. The unground anhydrite binder obtained at the temperature 800°C is a little bit smaller (specific surface area - 350 m^2/kg), than the one obtained at the temperature 900°C (specific surface area 300 m^2/kg) (Table 2). Its W/A ratio is high (0.55). Meanwhile the calcined material at the temperature 900°C has W/A equal to 0.37.

We can see from the results in Table 3 that upon grinding the latter material to (600 ± 10) m^2/kg, the less amount of water is required for obtaining the formation mixture of normal consistence (W/A ratio decreases from 0.37 to 0.29). The compressive strength of the samples of this anhydrite binder increases after 7 days as well as after 28 days of hardening.

Table 3. Compressive strength of hardened samples.

Mixture No	Temperature of calcination (ºC)	W/A	Compressive strength after hardening (MPa)			
			3 days	7 days	28 days	Dry samples*
1	800	0.34	-	-	9.51	15.44
2	800	0.34	7.44	9.01	10.86	15.76
3	800	0.34	10.07	12.48	15.17	23.82
4	800	0.34	2.21	4.49	8.57	13.15
5	800	0.34	-	-	7.33	12.60
1	900	0.29	-	5.16	15.72	16.24
2	900	0.29	7.98	9.51	16.18	18.52
3	900	0.29	11.67	16.06	18.75	30.74
4	900	0.29	13.14	14.95	16.80	24.78
5	900	0.29	8.31	9.09	13.16	18.73

* samples hardened in 90 % relative humidity environment for 28 days, afterwards desiccated
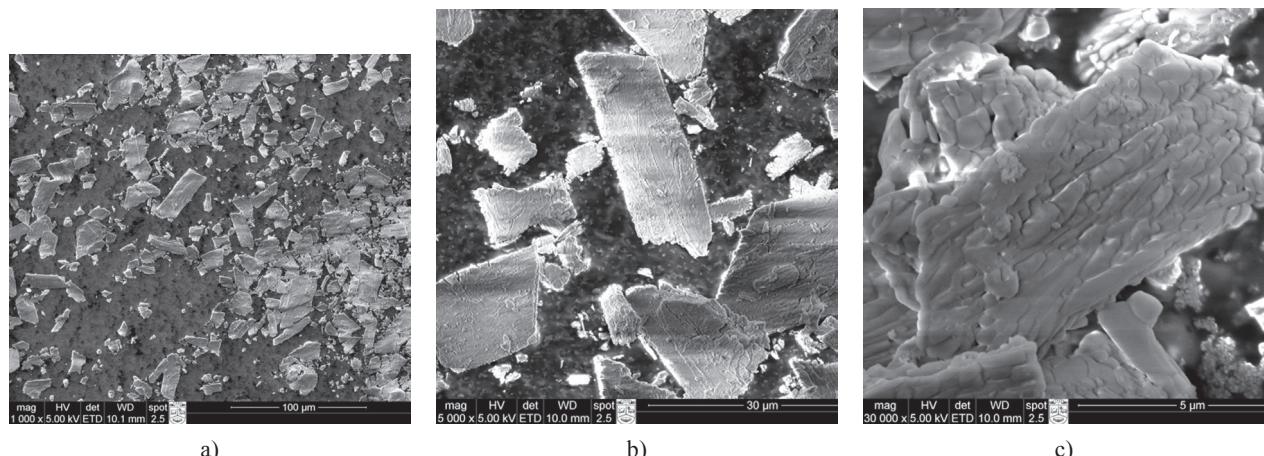

a)   b)   c)

Figure 6. SEM microphotographs of anhydrite binder calcined at temperature 800ºC: a, b, c - different magnification.
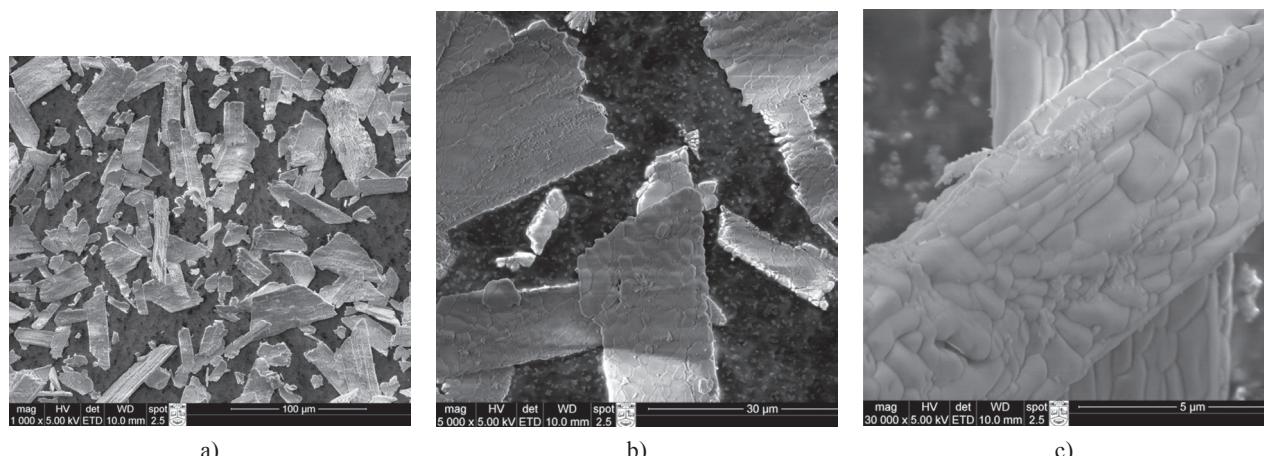

a)   b)   c)

Figure 7. SEM microphotographs of anhydrite binder calcined at temperature 900ºC: a, b, c - different magnification.

In general, it is possible state that the higher calcination temperature (900°C) and the grinding of the material (to specific surface area of 600 ± 10 m²/kg) improve the properties of anhydrite binder: fasten binding and increase the compressive strength (Tables 2, 3) in comparison with unground and calcined material at the temperature 800°C.

The analysis of the effect of the additives on the properties of the anhydrite binder (Tables 2, 3) shows that the binding of the calcined material with the additives of the dust from a cupola furnace and of the ground glass accelerates and the early compressive strength increases. This effect is stronger in the anhydrite binder calcined at the temperature 900°C than calcined at the temperature 800°C.

The additives used during the calcinations differ by an alkalinity. We can see from the data presented in Tables 2, 3 that the positive effect on the binding and on the hardening of the anhydrite is higher when additive of the ground glass is used, which has the higher alkalinity (pH 10.2 - 10.3) in comparison with the dust from cupola furnace (pH 9.1 - 9.2). It is possible to conclude that during the calcination of the phosphogypsum neutralized by lime to pH of 11.0-11.5 the calcium oxide [15], which presents in the system, as well as the alkaline compounds of Na^+, K^+, which present in the composition of the additives, act as the activators for binding the anhydrite. The hardening activators (Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $CaCl_2$ and others) used in practice for binding anhydrite

material form complex saline that enhance the hardening and improve the strength properties of the material [5, 6, 7, 11, 12, 13, 14].

We can see from the results presented in Tables 2, 3 that the samples produced from anhydrite binder calcined at the temperatures 800 and 900°C together with additives of 5 % clay and of 5 % ground glass bind and harden faster than without additives. The formed specimens from this composition of the anhydrite binder calcined at the temperature 900°C reach the early compressive strength - 13.14 MPa after 3 days. We can see from the X-ray diffraction pattern 2 presented in Figure 4 as well as from the data [16, 20] that the low amount the aluminosilicate of calcium: anorthite CAS_2 and gehlenite C_2AS come out. It is possible to conclude that hydration of them can reactivate the binding of the anhydrite binder and it can enhance the early strength. The hydration of anorthite and gehlenite invokes the formation of aluminosilicate hydrates of calcium (see Figure 8).

We do not provide the STA curves of hydrated anhydrite binder because they have the same form as provided in Figure 1b, the numbers are different only.

The enhancement of the compressive strength of the samples formed from the higher amount of the clay (10 %) and the same amount of the ground glass (5 %) delays in comparison with the samples formed from the anhydrite binder calcined together with the additives of 5 % clay and of 5 % ground glass within 28 days.
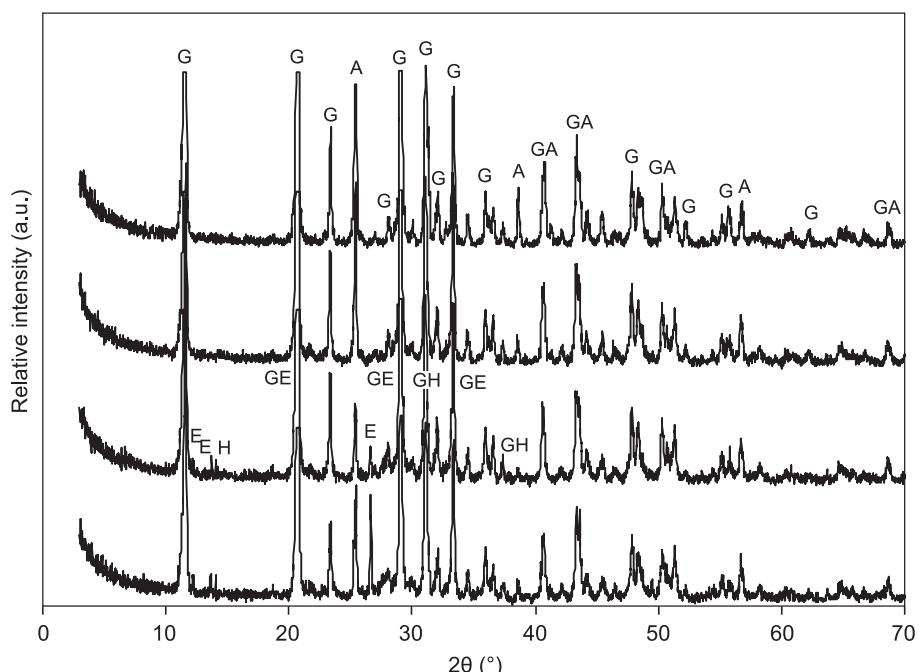

Figure 8. X-ray diffraction patterns of hydrated anhydrite binder: 1 - 1 mixture, 2 - 2, 3 mixtures, 3 - 4 mixture, 4 - 5 mixture. Composition of mixtures is reported in Table 1. Indexes: A - anhydrite $CaSO_4$; G - gypsum $CaSO_4·2H_2O$; E - gismondite $CaAl_2Si_2O_8·4H_2O$; H - calcium aluminium silicate hydrate $Ca_2Al_2SiO_7·8H_2O$

CONCLUSIONS

It was determined that the lime neutralized phosphogypsum with additives of the dust from cupola furnace, of the ground glass and of clay calcined at the temperature 900°C, and the following grinding of it to the specific surface area 600 ± 10 m²/kg allow obtaining the fast setting anhydrite binder.

The anhydrite binder with additive of 5 % ground glass exhibited the best physical and mechanical properties among all the investigated binders: its setting duration was 13 – 38 min; the compressive strength of the hardened dry samples was 30.74 MPa.

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