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INFLUENCE OF THE SETTING ACTIVATORS ON THE PHYSICAL MECHANICAL PROPERTIES OF PHOSPHOANHYDRITE

Article Highlights

- Phosphoanhydrite was obtained from neutralized phosphogypsum at temperatures 800 and 900 °C
- The properties of phosphoanhydrite were improved upon grinding it to surface area 600 m²/kg
- The properties of phosphoanhydrite were improved using setting activators K₂SO₄ and Na₂SO₄
- Syngenite and glauberite were formed in the samples with additives K₂SO₄ and Na₂SO₄
- The compressive strength of dry specimens was 58.5 MPa

Abstract

Phosphoanhydrite was obtained by processing dihydrate phosphogypsum generated during phosphoric acid production at Joint Stock Company (JSC), Lifosa (Lithuania). The influence on the properties of phosphoanhydrite of the treatment process parameters was determined, including: the conditions of phosphogypsum neutralisation in the lime suspension, temperature and duration of calcination of neutralized phosphogypsum to phosphoanhydrite, fineness of ground anhydrite, selection of additives activating the hydration of anhydrite and their amounts. Upon adding activators of anhydrite hydration, K₂SO₄ or Na₂SO₄, XRD and IR spectral analysis data show that the specimens, after 1 day of phosphoanhydrite hydration with additives, contained complex salts - syngenite upon using K₂SO₄ additive and glauberite in the case of Na₂SO₄ additive. These additives act as crystallization centers and accelerate hydration. It was determined that the specimens of phosphoanhydrite calcined at a temperature of 900 °C with 2% K₂SO₄ additive have the best physical and mechanical properties. Already after 1 day of hardening the specimens acquired a compressive strength of 21.18 MPa, and after 28 days of hardening they had a compressive strength of 58.5 MPa (dry specimens).

Keywords: neutralized phosphogypsum, phosphoanhydrite, dihydrate calcium sulphate, calcination, potassium sulphate, sodium sulphate.

Large underground layers of natural anhydrite can be found in Lithuania, but due to high depths (150–300 m) they are not quarried in practice. Natural sulphate raw material can be replaced with production waste. The production of phosphoric acid from natural phosphate rock by the wet process gives rise to an industrial by-product called phosphogypsum [1]. In

Lithuania, JSC Lifosa produces around 430 thousand tons of phosphoric acid per year and by 4–5 times more phosphogypsum, respectively, which usually is dumped in large stockpiles and causes serious environmental damage [2]. Its use in the production of building materials would be useful in terms of both ecology and economy.

The application of phosphogypsum in the production of binding materials is encumbered by phosphatic, fluorine and other soluble impurities in its content. In spite of that, some countries successfully use phosphogypsum raw material for the production of anhydrite cement [3–7]. In fact, the methods of wash-

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ing, thermal or chemical extraction of phosphogypsum impurities differ only. A possibility to use an unwashed and lime-neutralized waste phosphogypsum -calcium sulphate dihydrate - for obtaining an anhydrite binding material was determined in the studies of Lithuania's scientists [5,8,9].

Different authors have suggested different temperatures for the preparation of anhydrite binding material. Singh and Garg determined that a stable anhydrite could be produced by heating phosphogypsum at 1000 °C [3]. When heated at an elevated temperature, phosphogypsum produced an anhydrite, phosphatic and fluoride impurities became inert. As noted by the same authors [10], when phosphogypsum was calcined at 900-1000 °C to anhydrite and mixed with suitable chemical activators, it acquired high strength plaster, which is suitable for flooring tiles.

Activation of anhydrite cement can be increased upon grinding it with impurities [3,10,11] or dissolving activators in water during specimen formation [4,5,12,13]. Different researches analysed the impact of the following hardening activators: Na₂SO₄, K₂SO₄, (NH₄)₂SO₄, FeSO₄, CaCl₂ and K₂Cr₂O₇ [3-6,12-16].

It has been determined that hardening of the anhydrite binding material with the help of activators resulted in the formation of following complex salts: glauberite, magnesium sulphate hexohydrate, epsomite, which have a positive impact on the strength of specimens [16]. The research with activators K₂SO₄ confirmed that the hardening process of anhydrite cement was related with the formation of syngenite [13].

As the summary of references shows, an anhydrite binding material can be obtained from phosphogypsum upon removal of acid impurities (neutralizing or washing them), and afterward, upon calcination of the neutralised phosphogypsum to anhydrite and adding activators of anhydrite hydration.

The aim of this study is to determine the influence of the setting activators on the properties of phosphoanhydrite.

EXPERIMENTAL

Phosphogypsum (dihydrate calcium sulphate), a waste material of phosphoric acid production (from the Kola apatites) was the main material in the investigation. It was taken from the stockpiles of orthophosphoric acid production waste at JSC Lifosa. The average chemical composition of phosphogypsum (%) is: CaO - 31.90; SO₃ - 46.00; R₂O₃ - 1.02; total P₂O₅ - 0.60 (including water-soluble P₂O₅ - 0.10); F - 0.14; other - 0.40; loss on ignition - 19.69; insoluble in HCl -

0.25. The pH of phosphogypsum in aqueous suspension is 4.7-4.8.

Pure CaO was used for the neutralization of phosphogypsum (free CaO = 96%, specific surface area - 320 m²/kg, Reachim, Russia).

The additives, *i.e.*, chemical reagents used as the activators of anhydrite hardening are sodium sulphate (Na₂SO₄ % pure) and potassium sulphate (K₂SO₄ % pure).

The neutralized phosphogypsum was calcined in a muffle furnace at 800 and 900 °C with an isothermal exposure of 30 min.

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

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

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

The X-ray powder diffraction data were collected using a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered CuK α radiation and graphite monochromator, operating with the voltage of 30 kV and emission current of 20 mA. The step-scan covered the angular range 2-60° (2 θ) in steps of 2 θ = 0.02°.

FT-IR spectra were carried out using a Perkin-Elmer Spectrum GX FT-IR system. Specimens were prepared by mixing 1 mg of the sample with 200 mg of KBr. The spectral analysis was performed in the range of 4000-400 cm⁻¹ with spectral resolution of 1 cm⁻¹.

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

To determine the compressive strength of phosphoanhydrite, cube specimens, 2×2×2 cm³, were formed. The water consumption and binding duration of the formation mixture (of normal consistency) were determined according to the standard LST EN 196-3. The samples were hardened in 95±5 % relative humidity environment and compressed by press ELE automat.

RESULTS AND DISCUSSION

Phosphogypsum was neutralized in the lime suspension (lime/water ratio - 0.004) according to the methodology [8,9] to phosphogypsum pulp (suspension), pH 11.0-11.5, with water (W) to phosphogypsum (G) ratio *W/G* = 1. Neutralized phosphogypsum

was filtrated and dried at 100 ± 2 °C. Specific surface area - $392 \text{ m}^2/\text{kg}$.

As the XRD analysis of the neutralized phosphogypsum shows (Figure 1), dihydrate calcium sulphate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dominated in this material.

The XRD analysis of materials calcined at 800 and 900 °C shows that anhydrous calcium sulphate CaSO_4 - anhydrite dominates in all the products (Figure 2). The FT-IR spectra of the phosphoanhydrite are identical (Figure 3). They include absorption bands characteristic of insoluble anhydrite (at 675 , 614 and 595 cm^{-1}) only [17].

Consequently, calcined products are dominated by insoluble anhydrite, which, according to research findings, binds and hardens slowly.

The neutralized phosphogypsum calcined at the temperatures of 800 and 900 °C is characteristic of poor binding properties (Table 1) with its binding duration being very long. Phosphoanhydrite obtained at a temperature of 800 °C starts binding after 240 h and finishes bindings after 246 h. Anhydrite obtained at a higher temperature, 900 °C, starts to bind sooner: the beginning of binding - 144 h, the end - 168 h.

In order to learn the impact of the temperature of calcination on the properties of phosphoanhydrite, the research on the microstructure of the investigated material was carried out.

SEM photos (Figure 4) show that prismatic and rhombic (tabular) shape anhydrite crystals of irregular boundaries and stackings are formed. Anhydrite cal-

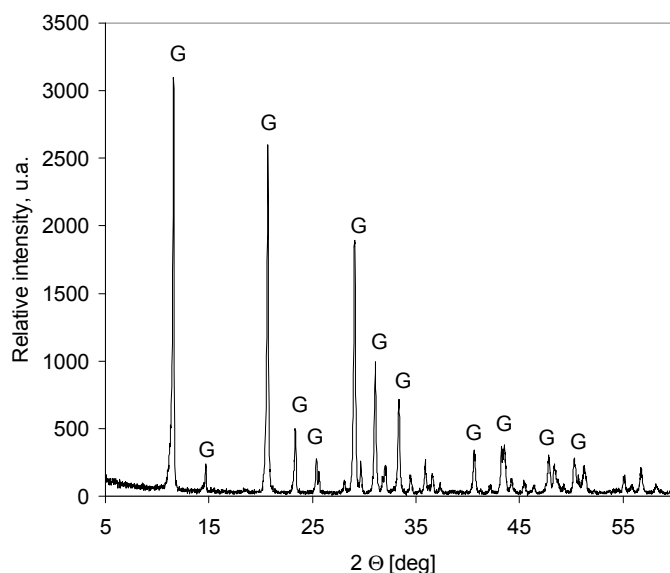


Figure 1. X-Ray diffraction pattern of the neutralized phosphogypsum ($G = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

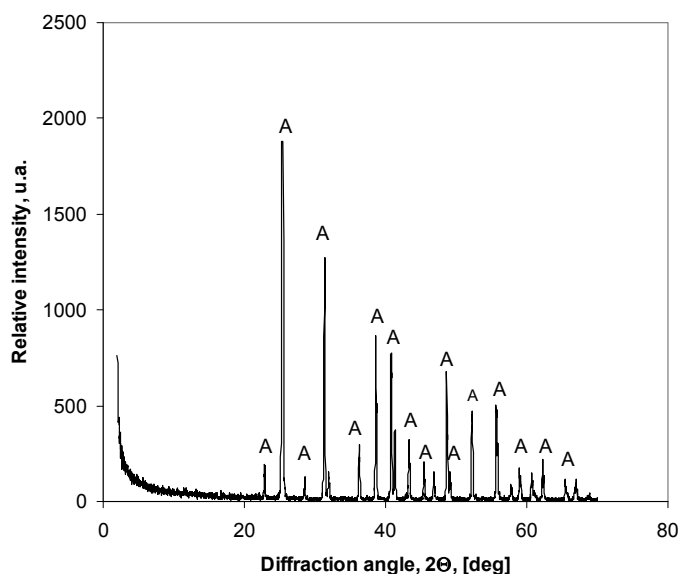


Figure 2. X-Ray diffraction pattern of phosphoanhydrite ($A = \text{anhydrite} - \text{CaSO}_4$).

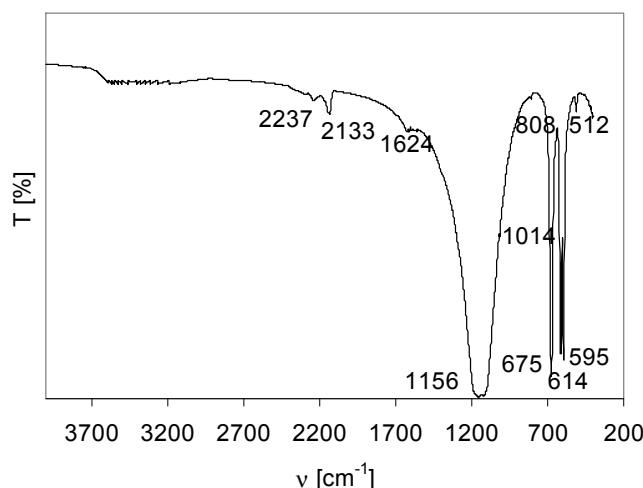


Figure 3. FT-IR Spectrum of the phosphoanhydrite.

Table 1. Characteristic properties of the phosphoanhydrite; W/A - water/phosphoanhydrite

Sample	Temperature of calcination, °C	Specific surface area, m ² / kg	W/A	Setting time, h/min	
				Initial	Final
1 ^a	800	350 ^a	0.55	240/00	246/00
1	800	600	0.41	10/10	11/30
1 ^a	900	300 ^a	0.37	144/00	168/00
1	900	600	0.29	5/50	8/30

^aNo grinded material

cined at 800 °C (Figure 4a) is distinguished by small-sized crystals of irregular arrangement. Their surface is crannied (Figure 4b). It is assumed that after crystal hydrate water disappears, micro crannies emerge in the crystal structure of the material in question. Meanwhile, the crystals of anhydrite calcined at 900 °C (Figure 4c and d) have a more even (smoother) surface without micro crannies, which are semi-melted. These crystals are larger and form hard sintered aggregates. Tabular microcrystal aggregates are predominant. The statement that a material calcined at 900 °C is harder as the duration of its grinding increased by 4 times (from 25-30 to 110-115 min) compared to that of a material obtained at 800 °C temperature was proved after grinding an anhydrite calcined at different temperatures to the specific surface area (600±10 m²/ kg).

Differences in the crystal structure can be explained by the properties of anhydrite calcined at different temperatures (Table 1). Phosphoanhydrite obtained at 800 °C is a bit finer (with a specific surface area of 350 m²/kg) compared to that obtained at 900 °C (with a specific surface area 300 m²/kg, Table 1). It has a high W/A ratio of 0.55. This material starts to bind only after 240 h (10 days). Meanwhile, the material calcined at 900 °C has a W/A ratio of 0.37, it binds and hardens quicker - the beginning of binding

is 144 h (6 days) and the end - 168 h (7 days). As the results presented in Table 1 show, after the latter material is ground to 600 m²/kg, less water (W/A ratio decreased from 0.37 to 0.29) is necessary to obtain a formation mixture of normal consistency. The compressive strength of ground phosphoanhydrite specimens (Table 2) is higher than that of unground after both 7 and 28 days of hardening.

In summary, it can be stated that a higher calcination temperature (900 °C) and material grinding (to specific surface area 600±10 m²/kg) improve (activate) the properties of anhydrite cement: accelerate binding and increase the strength of specimens (Tables 2 and 3) compared to the material calcined at 800 °C and unground. However, the duration of binding is still long (5-8 h), and the specimens acquire strength only after 3-7 days.

In order to activate the hydration of phosphoanhydrite, the impact of K₂SO₄ and Na₂SO₄ was analysed. These additives were inserted during specimen formation. The obtained results show decreased duration of binding of phosphoanhydrite calcined at both 800 and 900 °C (Table 3) and increased early compressive strength of the specimens (Table 2) when activators were used.

As data presented in Tables 2 and 3 shows the best result out of the selected hardening activators

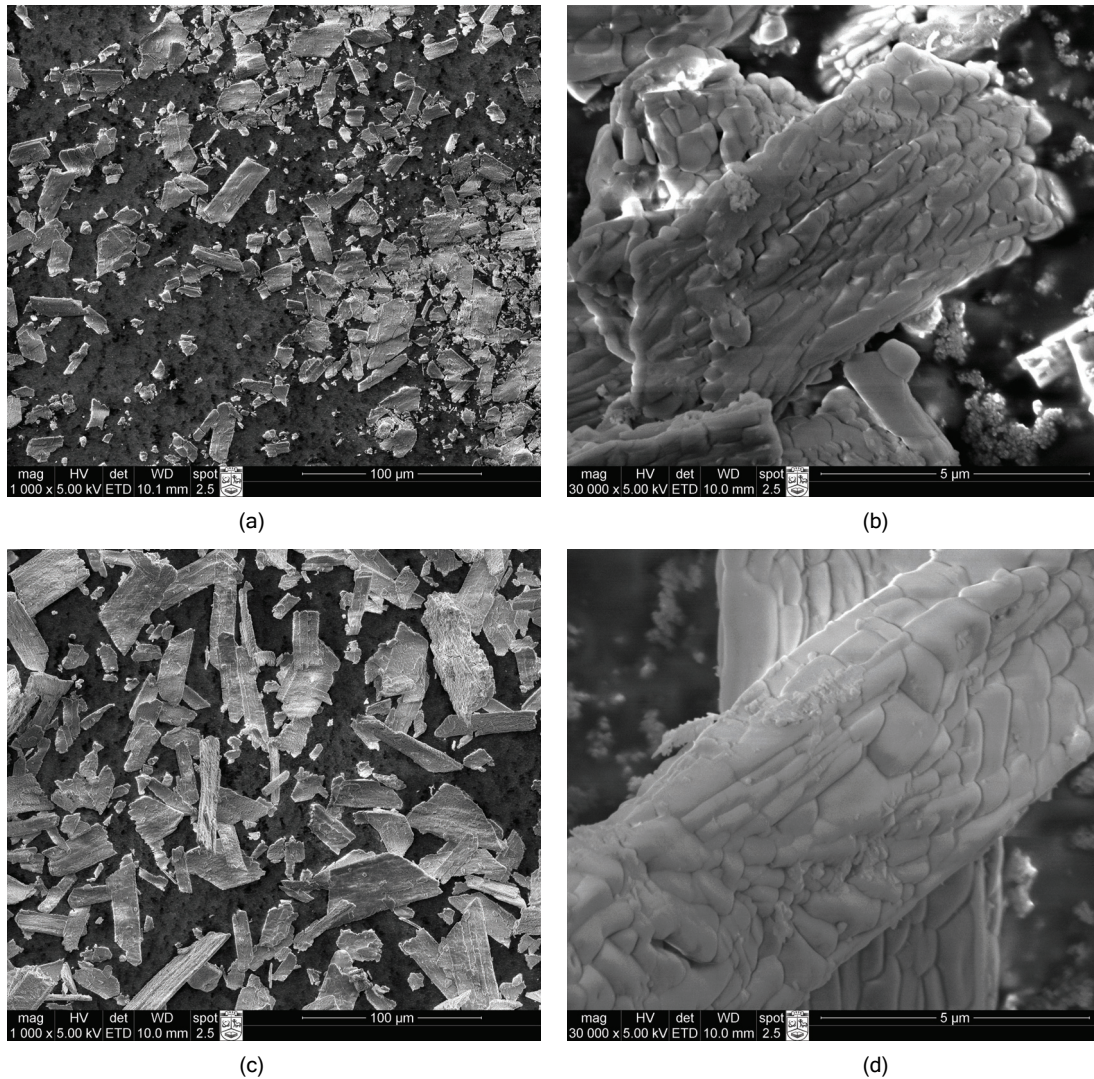


Figure 4. SEM Microphotographs of phosphoanhydrite calcined at temperatures of: a) and b) 800 °C; c) and d) 900 °C.

Table 2. Compressive strength properties of hardened samples

Sample No.	Specific surface area, m ² /kg	Content of additives, %		W/A	Compressive strength after hardening, MPa					
		K ₂ SO ₄	Na ₂ SO ₄		1 day	3 days	7 days	28 days	28 days, dry samples ^a	
Temperature of calcination 800 °C										
1	350	-	-	0.55	-	-	-	5.37	6.35	
2	600	-	-	0.41	-	-	-	12.25	15.73	
3	600	2.0	-	0.41	10.50	13.13	15.38	18.40	30.40	
4	600	4.0	-	0.41	The samples did not form					
5	600	-	2.0	0.41	9.33	10.80	13.48	17.53	20.18	
6	600	-	4.0	0.41	10.90	13.50	14.98	18.50	21.95	
Temperature of calcination 900 °C										
7	300	-	-	0.37	-	-	-	18.70	21.68	
8	600	-	-	0.29	-	2.10	3.88	36.85	56.90	
9	600	2.0	-	0.29	21.18	29.08	34.03	40.15	58.50	
10	600	4.0	-	0.29	The samples did not form					
11	600	-	2.0	0.29	18.95	20.43	24.48	27.55	46.00	
12	600	-	4.0	0.29	20.2	23.65	25.05	32.33	46.55	

^aSamples hardened in 95±5% relative humidity environment for 28 days, afterwards desiccated

Table 3. The influence of activators to the properties of ground phosphoanhydrite (600 m²/kg)

Sample No.	Content of additives, %		Temperature of calcination, °C					
	K ₂ SO ₄	Na ₂ SO ₄	800			900		
			W/A	Setting time, h/min		W/A	Setting time, h/min	
			Initial	Final		Initial	Final	
1	-	-	0.41	10/10	11/30	0.29	5/50	8/30
2	2.0	-	0.41	0/22	2/04	0.29	0/04	1/12
3	4.0	-	0.41	0/2	0/4	0.29	0/01	0/02
4	-	2.0	0.41	2/26	4/03	0.29	1/13	2/43
5	-	4.0	0.41	2/08	3/21	0.29	0/39	2/18

was produced by K₂SO₄ of 2%. A larger amount of this additive (4%) accelerates material binding up to 1-2 min and, therefore, attempts to form specimens failed (Table 2).

Specimens formed from phosphogypsum calcined at 900 °C temperature with 2% K₂SO₄ additive harden quicker and their compressive strength after 28 days of hardening is 2.9 times higher compared to the specimens made of phosphoanhydrite calcined at 800 °C temperature with the same amount of Na₂SO₄ additive. The compressive strength of these dry specimens reaches 58.5 MPa (Table 2).

The increase of Na₂SO₄ additive from 2 to 4% only slightly increases the compressive strength of the specimens of phosphoanhydrite calcined at both

800 and 900 °C. The compressive strength of dry specimens reaches 21.95 and 46.55 MPa, respectively.

It has been determined that the specimens of phosphoanhydrite calcined at a temperature of 900 °C with 2% K₂SO₄ additive have the best physical and mechanical properties. Already after 1 day of hardening these specimens acquired a compressive strength of 21.18 MPa, and after 28 days of hardening dry specimens had a compressive strength of 58.5 MPa.

The impact of hardening activators on the hydration of anhydrite can be explained by the formation of complex salts, glauberite - Na₂Ca(SO₄)₂ and syngenite - K₂Ca(SO₄)₂·H₂O, which were identified in XRD analysis (Figures 5 and 6). These salts were identified

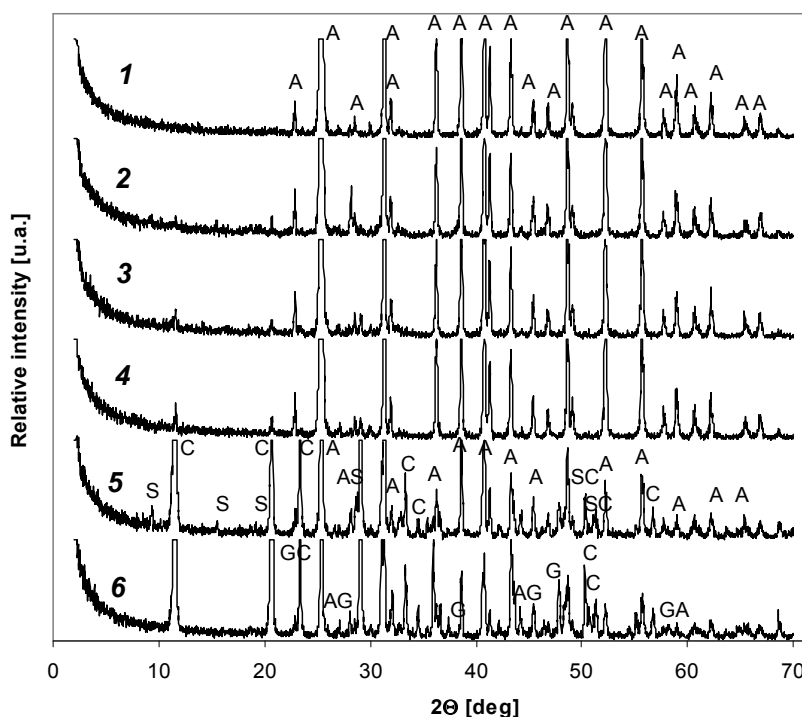


Figure 5. X-Ray diffraction patterns of phosphoanhydrite after 2 h (1-3) and 1 day (4-6) hydration: 1 and 4, without additives; 2 and 5, with 4% K₂SO₄; 3 and 6, with 4% Na₂SO₄; A = anhydrite - CaSO₄; C = gypsum - CaSO₄·2H₂O; G = glauberite - Na₂Ca(SO₄)₂; S = syngenite - K₂Ca(SO₄)₂·H₂O.

in the specimens of phosphoanhydrite calcined at both 800 and 900 °C after 1 day of hydration. Based on the data from the literature [18] it can be stated that the crystals of glauberite and syngenite with large specific surfaces act as crystallization centers pre-determining rapid hydration.

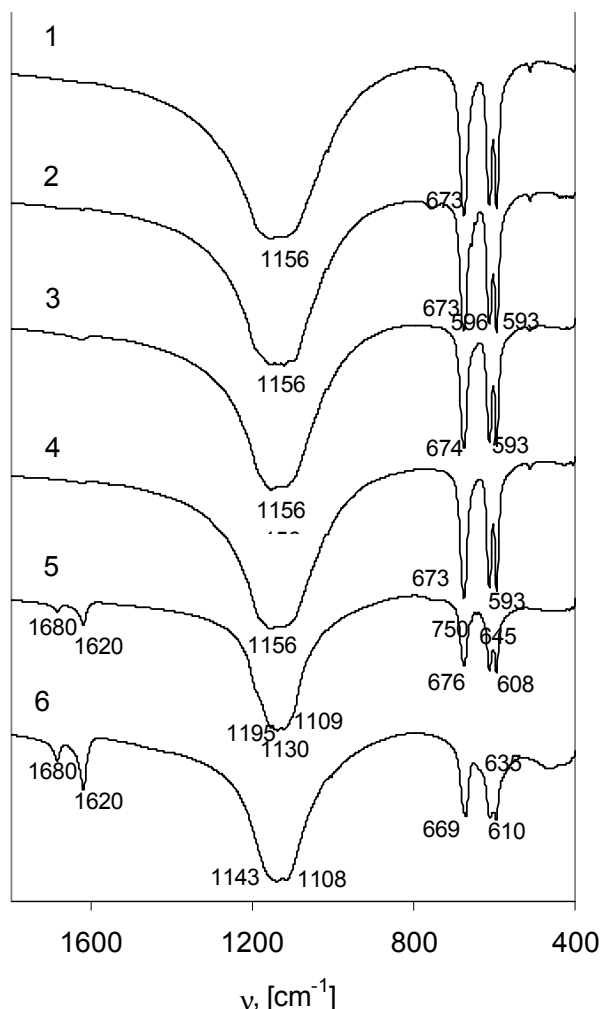


Figure 6. FT-IR Spectrum of the phosphoanhydrite calcined at 900 °C after 2 h (1-3) and 1 day (4-6) hydration: 1 and 4, without additives; 2 and 5, with 4% K_2SO_4 ; 3 and 6, with 4% Na_2SO_4 ; 1156, 673, 674, 596, 593 = anhydrite - $CaSO_4$; 1680, 1620, 1143, 1108, 676 = $CaSO_4 \cdot 2H_2O$; 635, 610 = glauberite - $Na_2Ca(SO_4)_2$; 1195, 1130, 750, 645, 608 = syngenite - $K_2Ca(SO_4)_2 \cdot H_2O$.

The formation of glauberite and syngenite during phosphoanhydrite formation is also confirmed by the IR spectral analysis (Figure 6). The spectra of phosphoanhydrite calcined at 800 and 900 °C with and without Na_2SO_4 and K_2SO_4 additives after 2 h and 1 day are similar. Since the hydration of phosphoanhydrite calcined at 900 °C is more rapid the spectra are better expressed. After 1 day of phosphoanhydrite

hydration with K_2SO_4 additive, syngenite forms with the following absorption bands: 1195, 1130, 750, 645, 608 (Figure 6, curve 5); and upon using Na_2SO_4 additive, glauberite forms - 635, 610 (Figure 6, curve 6) [13,19]. The aforementioned compounds are not identifiable after 2 h of hydration.

CONCLUSIONS

It has been determined that an anhydrite material with good binding properties can be obtained from JSC Lifosa phosphogypsum under the following conditions:

1. Upon neutralizing phosphogypsum in the lime suspension having pH 11-11.5.

2. Afterward, upon calcining it to anhydrite formation and finely grinding. It has been determined that the increase of calcination temperature of neutralized phosphoanhydrite from 800 to 900 °C and the grinding of material to specific surface area of 600 ± 10 m^2/kg improve the following properties of phosphoanhydrite: accelerate binding and increase the strength of specimens.

Upon adding activators of anhydrite hydration, K_2SO_4 or Na_2SO_4 , the data of XRD and IR spectral analysis show that the specimens after 1 day of phosphoanhydrite hydration with additives contain complex salts - syngenite upon using K_2SO_4 additive and glauberite in the case of Na_2SO_4 additive. These additives act as crystallization centers and accelerate hydration. It has been determined that the specimens of phosphoanhydrite calcined at the temperature of 900 °C with 2% K_2SO_4 additive have the best physical and mechanical properties. The compressive strength of dry specimens is up to 58.5 MPa.

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NAUČNI RAD

UTICAJ AKTIVATORA PODEŠAVANJA NA FIZIČKO-MEHANIČKA SVOJSTVA FOSFOANHIDRITA

Fosfoanhidrit je dobijen preradom dihidratnog fosfogipsa koji je nastao tokom proizvodnje fosfome kiseline u AD Līfosa (Litvanija). Određen je uticaj parametara procesa na svojstva fosfoanhidrita, uključujući uslove neutralizacije fosfogipsa u krečnoj suspenziji: temperatura i trajanje kalcinacije neutralisanog fosfogipsa do fosfoanhidrita, finoća samlevenog anhidrita, vrsta aditiva koji aktiviraju hidrataciju anhidrita i njihova količina. Nakon dodavanja aktivatora hidratacije anhidrita, K_2SO_4 ili Na_2SO_4 , rezultati dobijeni XRD i IR analizom pokazuju da uzorci nakon prvog dana hidratacije fosfoanhidrita sa aditivima sadrže složene soli - singenit u slučaju K_2SO_4 i glauberit u slučaju Na_2SO_4 . Ovi aditivi deluju kao centri kristalizacije i ubrzavaju hidrataciju. Utvrđeno je da uzorci fosfoanhidrita kalcinirani na temperaturi od 900 °C sa 2% K_2SO_4 imaju najbolje fizička i mehanička svojstva. Već posle jednog dana očvršćavanja uzorak je stekao kompresivnu čvrstoću od 21,18 MPa, a posle 28 dana očvršćavanja 58,5 MPa (suvi uzorci).

Ključne reči: neutralisani fosfogips, fosfoanhidrit, kalcijum-sulfat-dihidrat, kalcinacija, kalijum-sulfat, natrijum-sulfat.