INFLUENCE OF PHOSPHATIC IMPURITIES ON THE ANHYDRITE BINDING MATERIAL OF PHOSPHOGYPSUM

JURATE CESNIENE

Lithuanian Energy Institute, Breslaujos 3, LT-44403 Kaunas, Lithuania

E-mail: cesniene@mail.lei.lt

A possibility to use an unwashed, lime neutralized waste phosphogypsum - dihydrate calcium sulphate was analyzed in order to obtain an anhydrite binding material. Influence of calcination temperature on the properties of the obtained material was analyzed. It was determined that phosphoanhydrite calcined at 800°C temperature is characterized by optimal physical and mechanical properties. Temperature influence on the phosphatic impurities (hydroxyapatite) of neutralized phosphogypsum, which out of partially amorphous state transforms into the crystalline state, was analyzed. These impurities impede hydration and hardening processes. Waste phosphogypsum, in which P_2O_5 does not exceed 1.7 %, is needed to produce the binding material. In order to activate phosphoanhydrite binding properties, the influence of hardening activators was analyzed and their optimal amount was determined.

INTRODUCTION

Anhydrite binding materials are used world-wide in building material industry; however, their practical employment in Lithuania (and elsewhere) is impeded due to the fact that anhydrite is mined out of beds deep beneath the surface of the earth.

Phosphogypsum is a phosphoric acid production waste comprising up to 92-95 % of $CaSO_4 \cdot 2H_2O$. It has the same basic properties as natural gypsum and may be used as a substitute for natural gypsum and anhydrite in the manufacture of commercial construction products.

Manufacture of anhydrite cement from phosphogypsum is recommended [1]. On the investigations of durability, as compared to the plain hemihydrate plaster, anhydrite binding material shows much lower fall in strength and loss in weight [2].

Phosphogypsum raw material is successfully employed in a number of countries to derive the binding material [1, 3, 4]. Physical and chemical properties of these binding materials depend on the raw materials (apatites or phosphorites) and the methods used to produce phosphoric acid. Neutralization and extra treatment technologies of phosphogypsum impurities before the calcination differ radically [3, 4, 5].

The hydration kinetics of anhydrite obtained from phosphogypsum as well as that of anhydrite obtained from natural stone depends on the temperature of preparation, on the mechanical activation by grinding and chemical activators. It is determined [6] that when dihydrate calcium sulphate is calcined at 500-1000°C, structure and properties of the derived anhydrite differ significantly. At the increase of calcination temperature, material surface shrinks more than twice, a large amount of particles larger than 50 µm appear. According to other researchers' data [7, 8], the optimum of reactivity of synthetic orthorhombic anhydrite is observed in samples obtained by calcination at about 800°C. Data [1, 9] show that a stable anhydrite can be produced by calcinating phosphogypsum at 900-1000°C.

Two anhydrite hydration activation methods are proposed: the increase of anhydrite fineness by grinding and the usage of hardening activators.

The influence of grinding on anhydrite reactivity to water was investigated. The authors [10] investigated the evolution of microstructure and the rate of the conversion: $CaSO_4 \; II \rightarrow CaSO_4 \cdot 2H_2O$, as a function of grinding. It was established that the grinding operation causes important changes in the microstructure. The specific surface is always a function of the grinding time; and the reactivity of ground products is a function of a specific surface.

Since hardening activators are used for activating the consolidation of anhydrite from phosphogypsum, the system obtained is more complex. It has been proved that the activators affect the strength of the set anhydrite through their varying influence on anhydrite hydration [11]. Anhydrite hardening is precipitated by those additives which either precipitate the solid phase solubility or create conditions for the new hydration phase formation [12]. The additions of chemical activators increase the rate of dissolution of anhydrite for rapid transformation into hard strong gypsum matrix [9, 13]. Many researchers offer anhydrite hardening to

be activated with ordinary salts - K_2SO_4, $KAl(SO_4)_2 \cdot 12H_2O$, Na_2SO_4, $FeSO_4 \cdot 7H_2O$, $CuSO_4$, $ZnSO_4$, $NaHSO_4$ and other [1, 12, 14, 15] as well as with their complex compounds [7, 9, 12, 16]. However, when analyzing hydration processes of anhydrite obtained from phosphogypsum, the influence of phosphate and fluoride impurities should also be taken into account.

While either washing or neutralizing the phosphogypsum before the calcination, the most active impurities, which are phosphates and fluorides, influence the hydration and hardening processes of the obtained binding material. The effects of phosphates, fluorides and other impurities in phosphogypsum waste on the setting time, strength development and microstructure were studied [17]. The investigations showed that soluble phosphates retard the setting and strength development of plaster while soluble fluorides decrease the setting time and reduce the density and strength [18, 19]. However, there is little data on the influence of these impurities on the anhydrite binding material.

An innovative neutralization technology [5] of acid unwashed phosphogypsum from the Kola apatites enabling to effectively use this raw material in binding materials industry has been developed in Lithuania. It was determined [22] that that crystals of neutralized phosphogypsum are partially covered with $Ca_5(PO_4)_3 OH \cdot nH_2O$ - hydroxyapatite, which has a very small crystallization degree.

The objective of this work is to analyze a possibility to employ the unwashed and lime neutralized waste phosphogypsum in order to derive the anhydrite material and to determine the influence of phosphatic impurities on the properties of anhydrite material.

EXPERIMENTAL

Phosphogypsum - dihydrate calcium sulphate, waste material of phosphoric acid production (from the Kola apatites), was investigated. Dihydrate phosphogypsum was neutralized in lime suspension (water/lime ratio - 0.004) [5], desiccated and calcined for one hour at 400°C, 600°C and 800°C. The obtained material - phosphoanhydrite was grinded in a ball mill under the same conditions.

The key difference among phosphogypsum raw materials is the amount of phosphatic impurities having the biggest influence on the hydration properties of phosphoanhydrite binding material. Total amount of P_2O_5 (by weight) in tested materials was 0.4-2.5 %, the amount of fluorine - 0.1-0.2 %. The amount of P_2O_5 was determined according to LST EN 196-2 using the yellow phosphor-vanadium-molybdenum complex. Total amount of other components was analyzed by the complete chemical analysis according to LST EN 196-2.

An X-ray phase analysis was conducted using DRON-UM1 diffractometer (LOMO GUR-8 geometry). The investigation was carried out in the 2θ range from 10° to 60° with Ni-filtered Cu Kα radiation.

The microscopic analysis was conducted with scanning electron microscope JSM-5000 (SEM).

From the derived phosphoanhydrite sample - cubes (2 cm³) were prepared. Paste plasticity according Suttard (according to GOST 23789-79) was 18 cm. The samples were hardened in 95 ± 5 % relative humidity environment (till the proper time to determine compressive strength or hydration degree). After wet curing, the characteristics of their strength (or hydration degree) on dump samples (without desiccating) were determined. A specific surface area was determined according to the method of methyl red indicator absorption from benzene [20, 21].

Hydration degree (α) was determined on the same samples after compression strength testing after any hydration time of interest (1, 3, 5, 7, 14 and 28 days). The method of quantifying the degree of hydration of hardening phosphoanhydrite was performed as via measurement of its non-evaporable (chemically bounded) water content, following a procedure described elsewhere [23]. When achieving the required age, samples for the determination of non-evaporable water content were ground to powder, using a mortar and a pestle, and flushed with ethanol (100), using a porous ceramic filter and a vacuum, in order to halt the hydration. Filtered material was dried at 40°C, and then calcined at 400°C (according to GOST 23789-79). The non-evaporable water content was calculated as difference between the 40°C and 400°C mass measurements. To convert the non-evaporable water content measurements to estimated degrees of hydration, the non-evaporable water content for a fully hydrated sample was determined. The degree of hydration was then determined as the ratio of the measured non-evaporable water content per gram of phosphoanhydrite to the amount at full hydration.

RESULTS AND DISCUSSION

The influence of $Ca_5(PO_4)_3OH \cdot nH_2O$ - hydroxyapatite on the properties of phosphoanhydrite was investigated. The crystals of neutralized phosphogypsum are partially covered with hydroxyapatite having amorphous form. X-ray analysis shows, that the structure of phosphates synthesized at 20°C (Figure 1, the X-ray diffraction pattern 1) does not change when calcinating them up to 600°C (Figure 1, the X-ray diffraction pattern 2). However, when the temperature is increased up to 800°C, crystalline material β-$Ca_3(PO_4)_2$ is obtained (Figure 1, the X-ray diffraction pattern 3). This has been confirmed by microscopical analysis (Figures 2, 3) as well.

Some literary sources state [1] that phosphogypsum impurities, while phosphogypsum is being calcined at high temperatures (up to 1000°C), become inert, however, our research revealed that phosphatic impurities influence the hydration and hardening processes of anhydrite independent of phosphatic impurities state. The influence of those compounds on the properties of phosphoanhydrite is analyzed in this research.

Experiments reveal that properties of phosphoanhydrite derived from neutralized phosphogypsum depend a lot on calcination temperature. Taking into account different formation manner of phosphogypsum (if compared to natural raw material) and influence of phosphatic impurities we tried to calcinate the neutralized phosphogypsum at 400°C, 600°C and 800°C. After calcinating the neutralized phosphogypsum at 400°C, the performed X-ray analysis shows insignificant residual maximums, which belong to hemihydrate gypsum structure (Figure 4, the X-ray diffraction pattern 1), whereas key maximums, defining anhydrite structure, are less intensive, though material at this temperature was calcined for a long period of time - up to 15 hours

An in-depth analysis was carried out only with anhydrite derived after calcinating phosphogypsum at 600°C and 800°C. The X-ray analysis of these materials shows that they are both alike (Figure 4, the X-ray diffraction patterns 2 and 3), however, while investigating with microscope, different structure of crystals was observed (Figures 5, 6). Crystals of phosphogypsum calcined at 600°C (phosphoanhydrite - 600°C) are "porous", retaining overall spatial structure of former
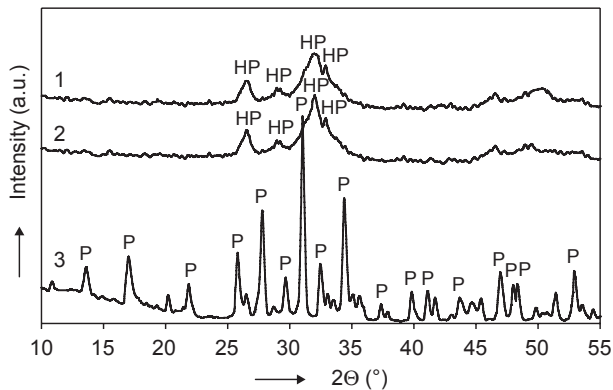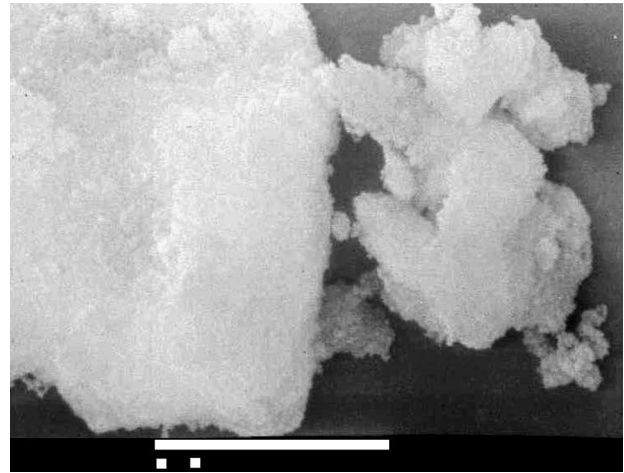

Figure 2. SEM micrograph of hydroxyapatite obtained in the laboratory and calcined at temperature 600°C.
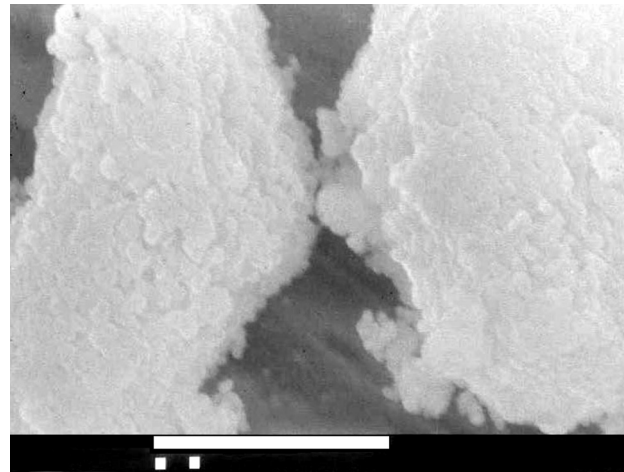
Figure 3. SEM micrograph of hydroxyapatite obtained in the laboratory and calcined at temperature 800°C.

Figure 1. The X-ray diffraction patterns of hydroxyapatite calcined at 20°C (1), 600°C (2) and 800°C (3); HP - $Ca_5(PO_4)_3OH \cdot nH_2O$, P - $\beta\text{-}Ca_3(PO_4)_2$.

Table 1. Physical-mechanical properties of phosphoanhydrite.

Calcination temperature (°C)	P_2O_5 (%)	Ratio W/A	Compressive strength (MPa)*	Specific surface area (m²/kg)
600	0.6	0.64	10.68	6540
600	1.2	0.64	10.45	6510
600	1.7	0.64	9.83	6920
600	2.5	0.65	9.81	7290
800	0.6	0.32	42.16	3740
800	1.2	0.32	38.14	3780
800	1.7	0.32	37.70	3870
800	2.5	0.32	35.70	3950
Natural anhydrite	-	0.30	26.60	3920

* Samples hardened in 95 ± 5 % relative humidity environment for 28 days, afterwards desiccated.

dihydrate crystal, whereas crystals of phosphogypsum calcined at 800°C (phosphoanhydrite - 800°C) are already indiscrete. This different structure of crystals, as research shows, mainly influences hydration and strength properties of phosphoanhydrite. Compressive strength of the samples, formed from phosphoanhydrite (600°), does not reach 11 MPa, whereas compressive strength of the samples, formed from phosphoanhydrite (800°C), is higher than 40 MPa (Table 1). Differences of crystals' structure explain a larger specific surface of phosphoanhydrite (600°C) - 6510-7290 m^2/kg, when compared to the specific surface of phosphoanhydrite (800°C) - 3740-3950 m^2/kg, (all investigated materials were ground at the same conditions), and water amount twice as large that is necessary for forming samples. A more dense and indiscrete structure of phosphoanhydrite (800°C) crystals determines higher strength of the samples.
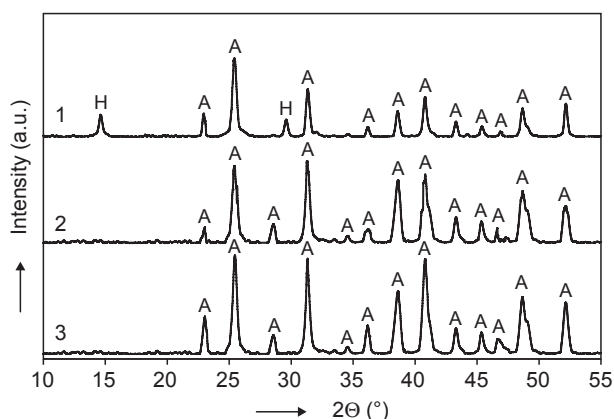
It was determined, that at the increase of the of phosphatic impurities amount from 0.6 % up to 2.5 % P_2O_5, compressive strength (after 28 days) of the samples from phosphoanhydrite (800°C) reduces approximately by 15 %, whereas compressive strength of the samples from phosphoanhydrite (600°C) diminishes only by 8 %. Obtained results show that in this case structural properties of the material have the greatest influence on the strength of phosphoanhydrite (600°C) but not on the amount of phosphatic impurities.

The analysis of kinetics of phosphoanhydrite (800°C) strength increase (Figure 7a) shows that a larger amount of phosphatic impurities has the greatest influence on impeding the strength increase during the period of the first seven days. At the increase of P_2O_5 from 0.6 % to 2.5 %, the initial strength reduces even by 60 %. The further increasing amount of phosphatic impurities does not impede the increase of strength so much. The influence of phopsphatic impurities, especially when their quantity is increased - 2.5 %, on strength increase is observed to be much lower during the hardening process of the phosphoanhydryte (600°C) (Figure 8a).

Figure 4. The X-ray diffraction patterns of neutralized phosphogypsum calcined at 400°C (1), 600°C (2) and 800°C (3); A - andydrite ($CaSO_4$), H - hemihydrate ($CaSO_4 \cdot 0.5H_2O$).
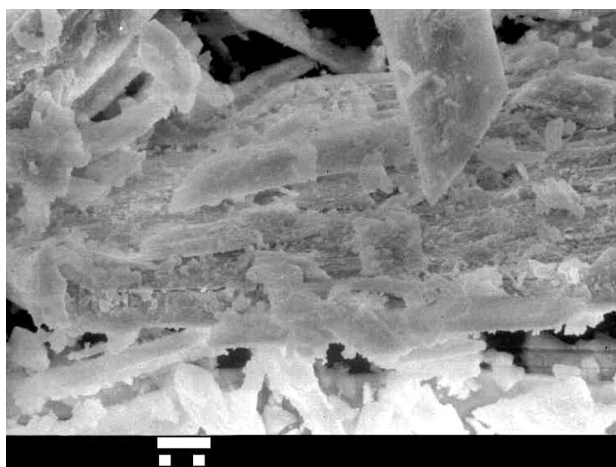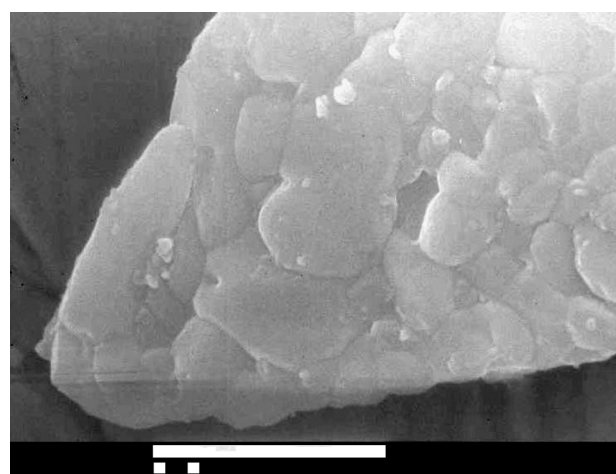

Figure 5. SEM micrograph of neutralized phosphogypsum calcined at temperature 600°C.
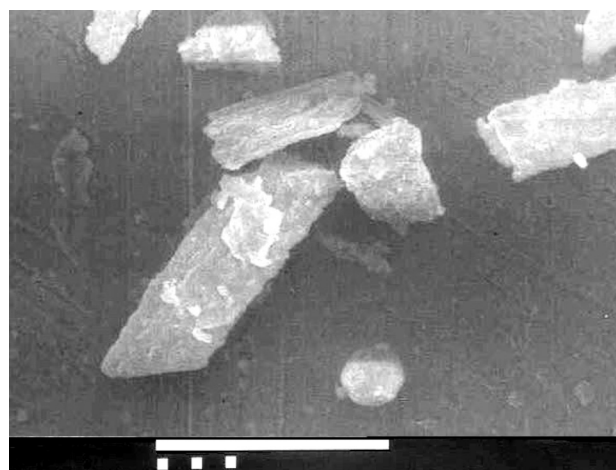

Figure 6. SEM micrographs of neutralized phosphogypsum calcined at temperature 800°C.

Figure 7. Influence of phosphatic impurities (P$_2$O$_5$ %) on the compressive strength a) and degree of hydration b) of phosphoanhydrite (800°C): O - 0.6 %; □ - 1.2 %; ◇ - 1.7 %; △ - 2.5 %; × - natural anhydrite.
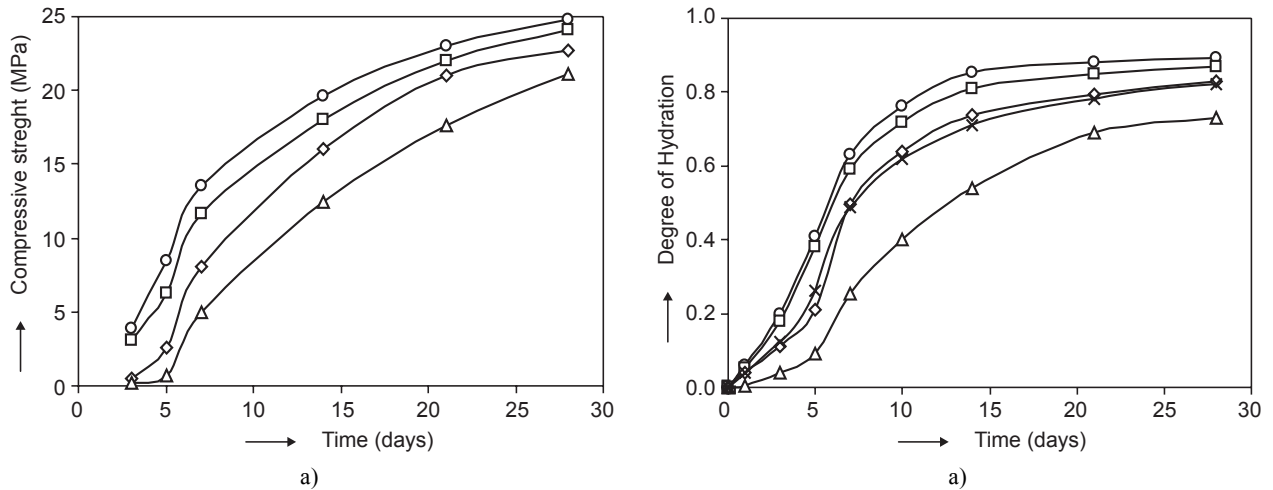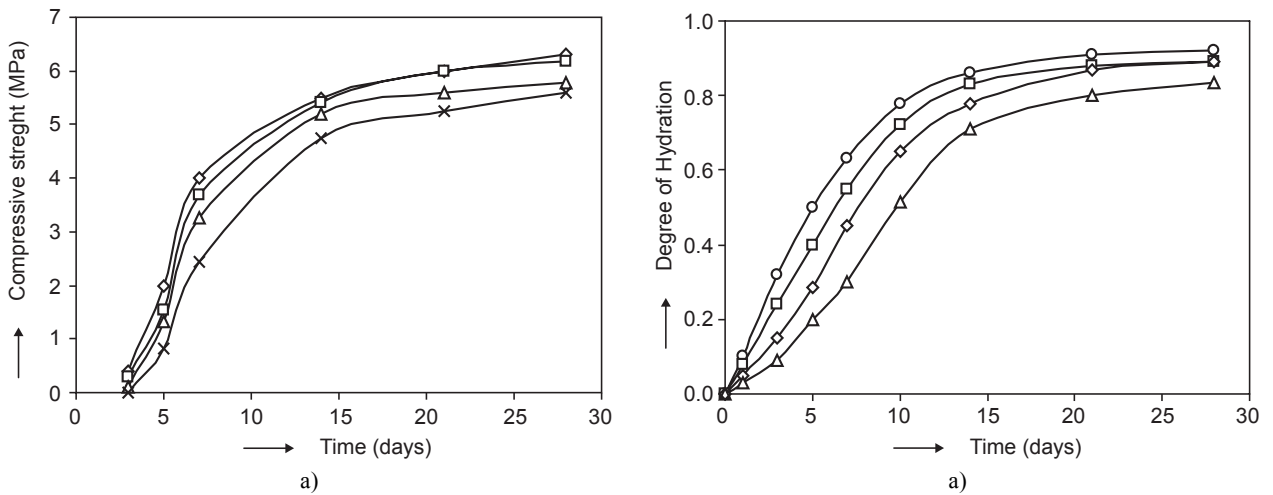

Figure 8. Influence of phosphatic impurities (P$_2$O$_5$ %) on the compressive strength a) and degree of hydration b) of phosphoanhydrite (600°C): ◇ - 0.6 %; □ - 1.2 %; △ - 1.7 %; × - 2.5%.

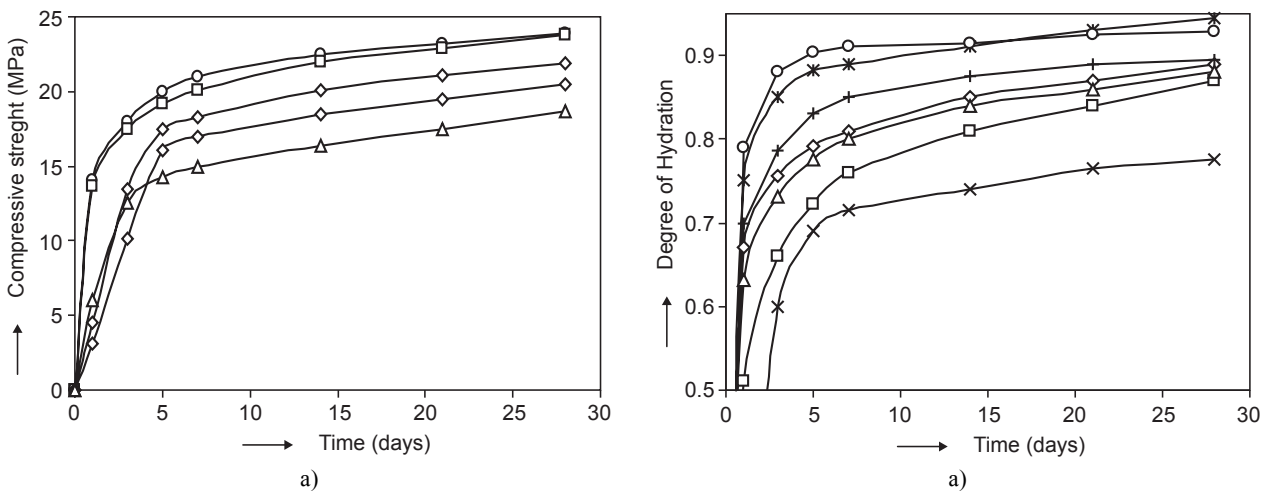Figure 9. Dependence of phosphoanhydrite compressive strength (a) and degree of hydration (b) on the amount of phosphatic impurities using activators: ◇, △, □, × - phosphoanhydrite (800°C) with 2 % K$_2$SO$_4$, P$_2$O$_5$ = 0.6 %; 1.2 %; 1.7 %; 2.5 %; ✱ - phosphoanhydrite (800°C) with 4% (NH$_4$)$_2$SO$_4$, P$_2$O$_5$ = 1.2 %; O, + - phosphoanhydrite (600°C) with 2% K$_2$SO$_4$, P$_2$O$_5$ = 1.2; 2.5 %.

Negative influence of the enlarged amount of phosphatic impurities was determined while analyzing the hydration process of phosphoanhydrite. Figures 7b and 8b reveal that the influence of these impurities is mainly expressed during the first 14-16 days, during the hydration of phosphoanhydrite (600°C and 800°C).

In this period hydration in both materials occurs almost under the same intensity. Further on, this process is more intensive in the material calcined at 600°C.

Investigation revealed that hydration rate of natural anhydrite, which was used for the testing (in the analyzed material there was ~ 10 % of dihydrate gypsum), and phosphoanhydrite (800°C) closely coincide, if the amount of P_2O_5 in the phosphogypsum is no greater than 1.7 %. If the amount of P_2O_5 is smaller than 1.7 %, hydration of phosphoanhydrite (800°C) proceeds more intensively than that of natural anhydrite. While comparing these two binding materials, it can be noticed that even though their dispersity is alike, however, the compressive strength of samples from phosphoanhydrite (800°C) is 1.5 times higher (Table 1).

Results of experiments show that when the neutralized phosphogypsum is being calcinated, a binding material, characterized by its good strength properties, may be obtained, however, its setting duration is very long (more than two days). Employment of hardening activators empowered to shorten the setting duration down to 3-6 hours. Several classical setting activators were chosen for the initial research. Research revealed that K_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$ greatly increase hydration process both of phosphoanhydrite (600°C) and phosphoanhydrite (800°C) (Figure 9b). It was determined that 2-4 % of the mentioned additives reduce the setting duration of phosphoanhydrite (600°C) down to 4-7 hours, hydration process itself increases 10-15 times during the first two days. However, porous structure of the material in this case determines a big W/A ratio and low strength: lower than that of the pure material - 5.0-9.6 MPa (after 28 days in dry condition), though hydration degree (α) reaches 0.9-0.92.

Figure 9 reveals that hardening activators increase phosphoanhydrite (800°C) hydration and hardening processes. K_2SO_4, Na_2SO_4 and $(NH_4)_2 SO_4$ enabled to shorten the setting period of the material down to 3-6 hours. It was determined that phosphatic impurities

(when there is more than 0.6 % P_2O_5) determine the deceleration of hydration and hardening processes (Figure 9) and partially (10-27 %) reduce the strength of dry samples (Table 2).

Compressive strength of samples, also taking into account the influence of phosphates, mostly depends on the selected calcification activator. Data presented in Figure 9a and Table 2 reveal that out of the chosen hardening activators, the best results were achieved by employing K_2SO_4. Though $(NH_4)_2SO_4$ is highest at reducing strength, however, paste plasticity increases significantly, therefore, this activator could be used as a plasticizer.

While comparing the data provided in Figures 7b, 8b and 9b, it is seen that phosphate impurities influence the hydration process of phosphoanhydryte even when hardening activators are used to enhance the hydration process. In this case the influence of the phosphate impurities is less evident when the quantity of P_2O_5 is higher. Increase of P_2O_5 quantity in phosphoanhydryte (600°C) from 1.2 % to 2.5 % retards the hydration of the material by 2.7 times during the first 24 hours; however, while the same materials hydrate with 2 % K_2SO_4, the hydration process retards only by 1.13 times. The same tendency may be observed when the phosphoanhydryte (800°C) is hydrating. During the first 24 hours the hydration rate of phosphoanhydryte (800°C) which contains 2.5% P_2O_5 decreases by 25 times, when compared with the material that contains 1.2% P_2O_5. When the same materials are used together with hardening activators, for example 2% K_2SO_4, and the quantity of phosphate impurities is higher during the first 24 hours, the hydration rate retards only by 3 times. While analyzing the presented data we see that with the right choice of hardening activators it is possible to decrease the negative impact of higher quantity of phosphate impurities on hydration characteristics of the materials.

When hydration activity and strength characteristics of the material were compared, it revealed that higher hydration degree does not always determine higher strength. When 2 % K_2SO_4 is employed and hydration degree is lower (α = 0.77-0.87), higher strength (34.5-42.1 MPa) of samples is obtained than using 4 % $(NH_4)_2SO_4$, when α = 0.89-0.94, and compressive strength is 27.6-33.8 MPa.

Table 2. Influence of setting activators on the properties of phosphoanhydrite (800°C).

| P$_2$O$_5$ (%) | Compressive strength (MPa)* | | | | | |
| | 2 % K$_2$SO$_4$ | | 2 % Na$_2$SO$_4$ | | 4 % (NH$_4$)SO$_4$ | |
	Dump samples	Dry samples	Dump samples	Dry samples	Dump samples	Dry samples
0.6	27.3	42.1	21.7	41.4	19.7	33.8
1.2	23.8	41.7	18.8	38.3	18.7	32.9
1.7	21.9	39.1	17.3	33.3	16.4	28.1
2.5	20.5	34.5	15.0	29.9	12.5	27.6
Natural anhydrite	14.7	30.1	12.7	25.3	12.8	26.6

* W/A of phosphoanhydrite- 0.35; natural anhydrite - 0.32.

The comparative experiments with natural anhydrite showed that employment of 2 % K_2SO_4, 2 % Na_2SO_4 and 4 % $(NH4)_2SO_4$ as setting activators is not enough in order to derive a natural binding material with good properties (rather long setting duration - beginning of setting starts only within more than 10 hours). In the analyzed case setting duration of phosphoanhydrite (800°C) is 3.5 times shorter, whereas compressive strength is 20-38 % higher.

CONCLUSIONS

1. A possibility to derive an anhydrite binding material (phosphoanhydrite) from the unwashed and lime neutralized dihydrate phosphogypsum was proved experimentally. It was determined that phosphoanhydrite properties mostly depend on the calcination temperature. The neutralized phosphogypsum calcined at 800°C is distinguished for the best physical and mechanical properties. Compressive strength of this binding material is running at 35-42 MPa.

2. Influence of temperature on the neutralized phosphogypsum phosphatic impurities - hydroxyapatite $(Ca_5(PO_4)_3OH \cdot nH_2O)$ was analyzed. It was determined that at 800°C hydroxyapatite from partially amorphous state transforms into crystalline state - β-$Ca_3(PO_4)_2$. Investigation revealed that these impurities impede phosphoanhydrite hydration and hardening processes. In order to produce a binding material, waste, where the amount of P_2O_5 would not exceed 1.7 %, should be used.

3. In order to activate binding properties of phosphoanhydrite and to hasten the hardening processes the influence of hardening activators K_2SO_4, Na_2SO_4 and $(NH4)_2SO_4$ was researched. It was determined that optimal amount of these activators is 2-4 %. Phosphate impurities influence the hardening process of phosphoanhydrite even when hardening activators are used.

References

1. Singh M., Garg M.: Cem.Concr.Res. *30*, 571 (2000).
2. Singh M., Garg M., Rehsi S.S.: Cem.Concr.Res. *20*, 271-276 (1990).
3. Sychova L. I. in: *Technology of Building Material and Construction*, P1, p.85-90, Belgorod 1995.
4. Lutz R.: ZKG International. *12*, 690, (1994).
5. Stonis S., Kaziliunas A., Vektaris B.: *The production of calcium sulphate β-hemihydrate*, USSA Pat. 1224287 (1986).
6. Hugo J. F., Guilhot B.: Cem.Concr.Res. *12*, 735 (1982).
7. Singh M., Rehsi S.S., Taneja C.A.: Zement-Kalk-Gips. II, *595* (1981).
8. Ouazzani Jamil A., Murat M., El Hajjouji A., Daviller D.: Cem.Concr.Res. *18*, 74 (1988).
9. Singh M., Garg M.: Constr.Build.Mater. *19*, 25 (2005).
10. Montanaro L., Delmastro A., Bachiorrini A.: Powder Technology. *52*, 93 (1987).
11. Israel D.: ZKG International. *04*, 228 (1996).
12. Fischer H.-B., Wtorov B. in: II International Conference on Chemical Technology of Cement. V 2, MUCTR, p.53-61, Moscow 2000.
13. Altmann H.-D.: Estrich-technik. *43*, 32 (1993).
14. Jarosiński A.: Cem.Concr.Res. *24*, 99 (1994).
15. Wtorov B., Fischer H.-B., Stark J. in: 14 Internationale Baustofftagung (14 ibausil), p.1069-1082, Weimar, 2000.
16. Singh M., Garg M.: Cem.Concr.Res. *25*, 332 (1995).
17. Singh M.: Constr.Build.Mater. *19*, 480 (2005).
18. Kaziliunas A., Leskeviciene V., Vektaris B., Valancius Z.: Chemical Technology. *9*, 38 (1998).
19. Singh M.: Cem.Concr.Res. *33*, 1363 (2003).
20. Shapiro J., Kolthoff I.M.: J.Am.Chem.Soc. *72*, 776 (1950).
21. Balthis J. H.: *Silica sols and preparation thereof from metallic silicon*, US Pat. 2614995 (1952).
22. Stonis S., Kaziliunas A., Vektaris B. in: *Building materials*, p.21-22, KPU, Kaunas 1982.
23. Bentz, D.P.: J.Am.Ceram.Soc. *80*, 3 (1997).

VLIV FOSFÁTOVÝCH PŘÍMĚSÍ NA ANHYDRITOVÉ POJIVO FOSFOSÁDRY

JURATE CESNIENE

Lithuanian Energy Institute,
Breslaujos 3, LT-44403 Kaunas, Lithuania

Byla zkoumána možnost používat nepromývanou, vápencem neutralizovanou odpadní fosfosádru - dihydrát síranu vápenatého pro získání anhydritového pojiva. Byl analyzován vliv kalcinační teploty na vlastnosti získaného materiálu. Bylo zjištěno, že as fosfoanhydrit pálený při 800°C se vyznačuje optimálními fyzikálními i mechanickými vlastnostmi. Dále byl analyzován vliv teploty na fosfátové příměsi (hydroxyapatit) neutralizované fosfosádry, která se kromě částečně amorfního skupenství přeměňuje také do krystalického stavu. Tyto příměsi brání hydrataci a procesu tvrdnutí. K výrobě pojiva je zapotřebí odpadní fosfosádra, v níž množství obsaženého P_2O_5 nepřesahuje 1,7 %. Byl zjišťován vliv aktivátorů tvrdnutí a jejich optimální množství pro aktivaci vazných vlastností fosfoanhydritu.