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HIGH-TEMPERATURE DECONTAMINATION AND UTILIZATION OF PHOSPHOGYPSUM

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Abstract. Waste piles of phosphogypsum formed from deposits of phosphoric acid production by-product loom near the city of Kėdainiai in the center of Lithuania. Every year about 250 thousand tons of this by-product were gathered when the plant was in full operation. At present, about 13 to 15 million tons of phosphogypsum have accumulated which is mainly gypsum dihydrate – (95–98) %, however, contaminated with phosphoric and fluoric acids as well as with other hazardous admixtures what makes this raw material ecologically harmful and also hampers the use of phosphogypsum instead of natural gypsum for the production of binding materials. These materials pollute the environment. Phosphogypsum can be „deacidified“ with lime and then treated as normal natural gypsum to obtain hemi hydrate gypsum. However, good-quality binding materials were not obtained in this case. Heating of phosphogypsum up to a temperature of 600 °C provides for the decomposition and elimination of binding obstruction admixtures. Heating to 1000 °C and higher temperatures causes the decomposition of the former with the formation of an activator in anhydrite lime and thus anhydrite cement. In general, the utilization of this environmentally harmful waste and the binding of toxic pollutants can contribute to the solution of environmental problems in the central region of Lithuania.

Keywords: detoxication, utilization, phosphogypsum, kaolin, high-temperature burning, binding materials.

1. Introduction

As various branches of industry – metallurgy, energy, construction materials, food and others as well as transport develop more and more harmful gases, such as CO_2, CO, SO_2, NO, NO_2, HCl, HF, not fully combusted hydrocarbons, also inorganic and volitile organic acids, organic solvents, the constituent parts of varnishes and paints – vapours and gases are emitted into the atmosphere.

Lithuanian researchers, including those from Vilnius Gediminas Technical University, Department of Environmental Protection, have conducted many investigations over the past years to evaluate various inert and toxic pollutant concentrations in the air [1–8], atmospheric precipitation [9] wastewater, in ponds and natural water basins and also in the soil [10–15]. All these data were compared by using instrumental methods, critically evaluated and a new generation of biofilters were developed which recommended themselves very well during further investigations [16–24].

Mineral fertilizer production is one of the branches of the chemical industry which emits hazardous materials into the environment, which are toxic to humans, fauna and flora. In 1963–1973 not far from the city of Kėdainiai in the center of Lithuania four sulphuric acid production lines were put into operation as well as those for the production of conventional and granulated superphosphate, aluminum fluoride, phosphoric acid, amofose and other fertilizer mixtures.

The main technological by-product produced at the Kėdainiai Chemical Plant (later Joint-Stock Company „Lifosa“) was phosphogypsum. It is formed during the manufacture of phosphoric acid by reacting the mineral apatite brought from Khibini region, Russia, with sulphuric acid according to the following reaction:

$$3Ca_3(PO_4)_2 \cdot CaF_2 + 10H_2SO_4 + 20H_2O = \\ 10[CaSO_4 \cdot 2H_2O] + 6H_3PO_4 + 2HF. \qquad (1)$$

Phosphogypsum is made up of (95–98) % of gypsum dihydrate $CaSO_4 \cdot 2H_2O$. Due to various admixtures, $CaCl_2$, SiO_2, $CaCO_3$, Al_2O_3, Fe_2O_3 which are present in apatite reaction with H_2SO_4 and H_3PO_4, a number of other compounds are formed like: $Ca(H_2PO_4)_2 \cdot H_2O$, HF, H_2SiF_6, HCl, $Ca_3(PO_4)_2$, $AlPO_4$, $FePO_4$, CaF_2, AlF_3, FeF_3, also small quantaties of apatite, magnesium, lanthanide compounds and various amounts of absorbed water are present.

Fig 1. Phosphogypsum waste piles near the city of Kėdainiai (author's photo)

After several decades of production thousands of tons of phosphogypsum have accumulated in waste piles not far from Kėdainiai.

Atmospheric precipitation has leached out many hazardous materials from these waste piles of phosphogypsum which entered the soil, then the surface water basins and ground water. Due to the influence of these pollutants surrounding trees looked like those in autumn with very little foliage. A little later, when air filters were installed in the production lines, the emissions into the atmosphere decreased.

Hydrogen fluoride (HF) is a colourless, volitile gas with a maximum admissible concentration (MAC) in the air of 0,5 mg/m^3. In the case of phosphoric acid MAC is a little higher and equal to 1 mg/m^3. So we can conclude that these substances are rather toxic, and their presence in phosphogypsum as well as during production and in waste piles is hazardous to humans, the environment and especially to vegetation.

The presence of acidic admixtures H_3PO_4, HF, H_2SiF_6 does not allow to reuse this by-product for structural gypsum production without any reprocessing.

The methods of low-temperature reprocessing evolve deacidification (neutralization) by lime (a slurry in water works best) at ambient temperatures. During the process $Ca(OH)_2$ neutralizes acidic admixtures, and insoluble precipitates are formed:

$$3Ca(OH)_2 + 2H_3PO_4 = Ca_3(PO_4)_2 \times mH_2O + (6 - m)H_2O. \qquad (2)$$

The method of high-temperature phosphogypsum reprocessing is based on phosphogypsum thermal treatment after which: 1) dihydrate gypsum transforms into anhydrite, and CaO is formed little by little; 2) hazardous admixtures ($H_3PO_4 \cdot H_2SiF_6$, HF) decompose and evaporate.

The following transformations occur:

1) dihydrate gypsum (120–160) °C transforms to a- or b-hemi hydrate, while at (170–220) °C α- or β- soluble anhydrite, the latter at > 400 °C changes to an insoluble form which without an activator (e g CaO) does not harden, but at 800 °C transforms into hydraulic gypsum, possessing enough CaO for binding to occur:

$$(n+1)\ CaSO_4 = n\ CaSO_4 + CaO + SO_2 + 0{,}5\ O_2. \qquad (3)$$

It is inexpediant to heat the substance during production of anhydrite binding materials to full decomposition because over-heated anhydrite is obtained. That is why it is enough to continue heating until, for example, 5 % of active CaO is formed.

Phosphogypsum reprocessing and usage possibilities were investigated since 1964 (Kaunas Polytechnical Institute, J. Kapačiauskas) and many other researchers from Kaunas Polytechnical Institute, Institute of Thermal Insulation as well as Institute of Architecture and Construction, whose names should be mentioned (in an alphabetical order): Andriušienė J., Bačauskienė M., Česnienė J., Kaminskas A., Kaziliūnas A., Leškevičienė V., Mandeikytė N., Martusevičius M., Nizevičienė D., Palubeckienė V., Rakaitis J., Sasnauskas K., Stonys S., Urbonas Z., Valančius Z., Vektaris B.

The main publication concerning this period are given in references [22–30].

Joint-Stock Company „Palemono keramika" during the period 1989–1992 and in 1997 manufactured a novel anhydrite cement composition according to the technology developed by Institute of Architecture and Construction [23]. This material was produced from the following raw materials: JSC „Lifosa" (Kėdainiai) dihydrate non-acidic phosphogypsum (pH = 9,8–9,3) – (79,0–79,5) %; Krūnas deposit clay – 16 %; neutralized JSC „Ekranas" (Panevėžys) glass slime (kinescope glass polishing waste) containing SiO_2 and R_2O – 4 %; $Ca(OH)_2$ from JSC „Ventos SM" –(0,5–1,0) %; water. Here phosphogypsum was neutralized with slaked lime until pH = 6,5–9,5 was reached, then clay and glass slime was introduced, water was added and the obtained slip was burnt in a rotary kiln at (850 – 900) °C. The obtained granulate had the following chemical composition: CaO – (25–33) %; SO_3 – (27–41) %, R_2O –(9,15–9,35) %, P_2O_5 – (0,52–0,75) %, F – (0,03–0,06) %; SiO_2 and insoluble part – (15–32) %. In such a way the anhydrite part makes up (46–70) %. The milled granulate possesses the following physico–mechanical properties: setting of binder – (40–135) min.; binding end – (135–230) min., flexural strength: after 3 days < 2MPa, after 28 days (3–4,5) MPa; compressive strength: after 3 days (5–7) MPa, after 28 days (16–30) MPa.

Unfortunately, very little attention was paid to high–temperature reactions of phosphogypsum containing CaO with acidic oxide SiO_2 (e g kaolin). Meanwhile, the CaO–SiO_2 interaction can give dicalcium silicates, also tricalcium silicates with distinguished binding properties.

The aim of this investigation was to examine the materials binding possibility and properties obtained from phosphogypsum and kaolin by heating then up to 1200 °C.

Also, the hazardous materials present in phosphogypsum waste piles are constantly leached out by the atmospheric precipitation into the environment and pollute the soil. That is why investigations concerning the utilization of harmful waste into useful binding materials will contribute to the solution of environmental problems of the central region of Lithuania.

2. Experimental investigation

The following materials were used in the experiments.

Phosphogypsum. The average chemical composition, %: Ca^{2+} 17,05; SO_4^{2-} 40,18; PO_4^{3-} 1,16; F^- 0,11; SiO_2 0,33; Fe^{3+} 0,002; H_2O 40,72; pH =2,47. If we express the composition in moles then we obtain the following: Ca^{2+} 0,426; SO_4^{2-} 0,419; PO_4^{3-} 0,01; F^- 0,006; SiO_2 0,005; H_2O 2.26. From here follows that we get the following molar composition: $CaSO_4 \times 2H_2O$ – 1 mole; Ca in other materials (phosphate, fluoride, etc.) – 0–0,016 mole; absorbtion water – 3,36 mole.

To evapourate absorbed water phosphogypsum was heated in a drying kiln at 105 °C for 2 days (till constant weight).

Kaolin. Kaolin used in the experiments was obtained from a laboratory in the Department of Geotechnical Engineering of VGTU. The dried material had the following chemical composition: (38,5–39,2) % Al_2O_3 and (45,4–46,3) % SiO_2, which is approximately close to the kaolinite formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. During the experiments the material was ground and dried additionally.

3. Testing methods

- The quantative determination of CaO, Al_2O_3 and SiO_2 in the material was conducted according to the methods given in Lithuanian Standard LST EN 196–2–Cement. Testing methods – Parts 2 (Chemical analysis – 13.12). Vilnius LSD publishing house, 1996.
- Burning of the phosphogypsum and kaolin mixture was conducted in a high-temperature furnace „Thermolyne Furnace 6000“ (up to 1200 °C).
- Experimental thermograms were obtained by using a derivatograph Q–1500.
- X-ray diffraction pattern analysis of heated products was conducted by using the X-ray difractometer DRON-2 (Russia) (Co anode, Fe filter, slits – 1 : 2 : 0,5 mm, the difractometer tube's operating mode: $U = 3$ kV, $I = 10$ mA).
- Measurements of specimen flexural and compressive strength were conducted by using conventional resistance measurement instruments according to the Lithuanian Standard LST 1346:1995 – Construction Mixtures (Technical requirements) by using 40×40×160 mm dimension prisms.

4. Results and discussion

4.1. Thermodynamic analysis of anhydrite thermal decomposition

It was demonstrated [27] that we could find the thermal treatment temperature to form necessary CaO amount in heated anhydrite according to thermodynamic calculations based on the following reaction:

$$CaSO_4 = CaO + SO_2 + 0{,}5\ O_2. \qquad (4)$$

If we adopt that the general evolved gas pressure during the reaction P, atm is equal to SO_2 and O_2 partial pressure p, atm sum, then we get: $P = p_{SO_2} + 0{,}5\ p_{O_2}$ and $P = 1{,}5\ p_{SO_2}$ From here we obtain the equilibrium constant $K_p = 0{,}385p^{1{,}5}$ and $\lg K_p = -0{,}4145 + 1{,}5l\ gP$.

When we insert this $\lg K_p$ value into the Gibb's energy change ΔG_T^o dependency on K_p equation $\Delta G_T^o = -4{,}575 \cdot 10^{-3}\ T \cdot \lg K_p$, we obtain: $\lg P = 10{,}112 - 17653/T$ and $T = 17653/(10{,}112 - \lg P)$.

Since the anhydrite CaO amount (in unit parts) is proportional to P, atm, then we find: $T = 17653/(10{,}11 - \lg CaO)$.

Then we find in such a way, e g to obtain 5 % of free CaO material, it is necessary to sinter the material at almost 1300 °C (Table).

4.2. Decomposition of phosphogypsum admixtures during heating

Unneutralized phosphogypsum contains besides gypsum: 2 % of apatite; (1,8–5,7) % of Ca; Al and Fe phosphates as well as fluorides; > = 1 (up to 6) % H_3PO_4; (0,3–10) % SiO_2; (7–22) % H_2O [26].

Amount of CaO in phosphogypsum depending on temperature

CaO, %	0,1	1	2	5	10	25	50	75	100
CaO, %/100	0,001	0,01	0,02	0,05	0,10	0,25	0,50	0,75	1,00
T, ° K	1346	1457	1494	1547	1589	1648	1695	1724	1746
t, ° C	1073	1184	1221	1274	1316	1375	1422	1451	1473

Gypsum binding properties are mostly hampered by the presence of HF, H_3PO_4 and $Ca(H_2PO_4)_2 \cdot 2H_2O$. Thermal treatment of phosphogypsum decontaminates it.

Hydrogen fluoride is dissolved in moisture present in phosphogypsum, and when it is heated at > 100 °C temperature, water evaporates.

Phosphoric acid during heating transforms into pyrophosphorous (diphosphoric) acid:

$$2H_3PO_4(>215\ °C) = H_4P_2O_7 + H_2O. \qquad (5)$$

The later polymerisizes into polymetaphosphoric acid:

$$(n = 3 - 8):\ n\ H_4P_2O_7(>300\ °C) = 2(HPO_3)_n + n\ H_2O.$$

During heating of this compound it evolves P_2O_5 vapours:

$$2(HPO_3)_n = nP_2O_5 + nH_2O. \qquad (6)$$

So, in such a way phosphoric acid present in phosphogypsum waste during burning completely decomposes and it evolves as P_2O_5 and H_2O.

Calcium dihydrophosphate present in phosphogypsum decomposes [6] as follows:

$$Ca(H_2PO_4)_2 \cdot H_2O\ (100 - 110\ °C) = Ca(H_2PO_4)_2 + H_2O, \qquad (7)$$

$$2\ Ca(H_2PO_4)_2(150 - 200\ °C) = Ca_2P_2O_7 + P_2O_5 + 4H_2O. \qquad (8)$$

Calcium dihydrophosphate present in phosphogypsum dissociates in the same way as phosphoric acid when phosphogypsum is heated.

- **pH-metric analysis of burnt phosphogypsum**

Our pH-metric investigations [26] have shown that untreated phosphogypsum saturated solution samples showed an increase in pH value with an increase in thermal treatment temperature (see values t °C/pH): 105/3,02; 200/3,02; 300/3,80; 400/3,90; 500/4,80; 600/5,78; 650/5,89; 700/6,04; 750/6,18; 800/6,26; 900/6,32; 1000/6,44.

Such a course of pH value change can be explained by the decomposition of the heated product at different temperatures:

1) At (100–200) °C – water is liberated; 2) (200–300) °C – water evolves from H_3PO_4 and $Ca(H_2PO_4)_2$; 3) (300–450) °C the $Ca(H_2PO_4)_2$ decomposition ends; 4) (450–600) °C diphosphoric and latter polymetaphosphoric acid decomposes with the emission of P_2O_5, 5) (> 600 °C) – the formation of inactive anhydrite takes place.

Phosphogypsum calcined up to 1000 °C contains very little amount of admixtures, which practically have no effect on the product's binding properties (compound and melting temperature, °C): FeF_3 1027; AlF_3 1040; $Ca_3P_2O_7$ 1350; CaF_2 1403; $Ca_3(PO_4)_2$ 1670; SiO_2 1728; $AlPO_4$ 2000.

4.3. Binding properties of phosphogypsum sintered up to 1000 °C

Our experiments [28] have shown that phosphogypsum heated in the temperature range (600–800) °C with an addition of 6 % of $Ca(OH)_2$ gave specimens with a flexural strength (0,3–2,2) MPa and compressive strength (0,4–1,2) MPa.

Materials prepared in these conditions distinguish themselves by low anhydrite cement strength properties and can be used for conventional purposes.

4.4. Preparation possibilities of binding materials from high-temperature interaction of phosphogypsum and kaolin

Partial decomposition of $CaSO_4$ begins at 960 °C in phosphogypsum during its burning and is associated with the formation of CaO (in the presence of SiO_2 or Al_2O_3, this decomposition begins at lower temperatures).

The calcination of kaolin (white clay) which is mainly composed of kaolinite $Al_4[Si_4O_{10}](OH)_8$ (in the oxide expression form – $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ and in the silicate chemistry accepted form – AS_2H_2), (500–600) °C gives metakaolinite as the resulting product AS_2; (1000–1200) °C – sillimanite AS and (1200–1500) °C – mullite A_3S_2 (here the following abbreviations are used: A – Al_2O_3, C – CaO, H – H_2O, S – SiO_2).

So we can state that during the calcinations of phosphogypsum and kaolin we can anticipate a number of interactions. Let us take a look at possible ones during which substances with various composition are formed.

1) Formation of calcium and aluminium silicates:

C/K = 1:

$$CaSO_4 + [Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = [CaO \cdot SiO_2] + [Al_2O_3 \cdot SiO_2] + 2H_2O + SO_2 + 0{,}5\ \ O_2,\ T_r > 891K \qquad (9)$$

C/K = 1,33:

$$4CaSO_4 + 3[Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = 4[CaO \cdot SiO_2] + [3Al_2O_3 \cdot 2SiO_2] + 6H_2O + 4SO_2 + 2O_2,\ T_r > 973K \qquad (10)$$

C/K = 1,5:

$$3CaSO_4 + 2[Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = [3CaO \cdot 2SiO_2] + 2[Al_2O_3 \cdot SiO_2] + 4H_2O + 3SO_2 + 1{,}5O_2,\ T_r > 1020\ K \qquad (11)$$

C/K = 2:

$$2CaSO_4 + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = [2CaO \cdot SiO_2] + [Al_2O_3 \cdot SiO_2] + 2H_2O + 2SO_2 + O_2,\ T_r > 1126\ K \qquad (12)$$

C/K = 2,5:

$5CaSO_4 + 2[Al_2O_3 \cdot 2SiO_2 – 2H_2O] = [3CaO \cdot SiO_2] + [2CaO \cdot SiO_2] + 2[Al_2O_3 \cdot SiO_2] + 4H_2O + 5SO_2 + 2{,}5O_2$, $T_r > 1220$ K (13)

C/K = 3:

$3CaSO_4 + [Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = [3CaO \cdot SiO_2] + [Al_2O_3 \cdot SiO_2] + 2H_2O + 3SO_2 + 1{,}5O_2$, $T_r > 1291$ K (14)

2) Formation of calcium alumosilicates

C/K = 1 (anorthite):

$CaSO_4 + [Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = [CaO \cdot Al_2O_3 \cdot 2SiO_2] + 2H_2O + SO_2 + 0{,}5O_2$, $T_r > 816$ K (15)

C/K = 2 (helenite):

$2CaSO_4 + [Al_2O_3 – 2SiO_2 – 2H_2O] = [2CaO \cdot Al_2O_3 \cdot SiO_2] + SiO_2 + 2H_2O + 2SO_2 + O_2$, $T_r > 1060$ K (16)

C/K = 3 (helenite):

$3CaSO_4 + [Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = [2CaO \cdot Al_2O_3 \cdot SiO_2] + [CaSO_4 \cdot SiO_2] + 2H_2O + 3SO_2 + 1{,}5O_2$, $T_r > 1060$ K (17)

C/K = 3,5 (grossularite):

$7CaSO_4 + 2[Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = [3CaO \cdot Al_2O_3 \cdot 3SiO_2] + [3CaSO_4 \cdot SiO_2] + [CaO \cdot Al_2O_3] + 4H_2O + 7SO_2 + 3{,}5O_2$, $T_r > 1275$ K (18)

3) Calcium silicate and alumosilicate formation

C/K = 4:

$8CaSO_4 + 2[Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = 2[3CaO \cdot 2SiO_2] + 2[CaO \cdot Al_2O_3] + 4\ H_2O + 8SO_2 + 4O_2$, $T_r > 1275$ K (19)

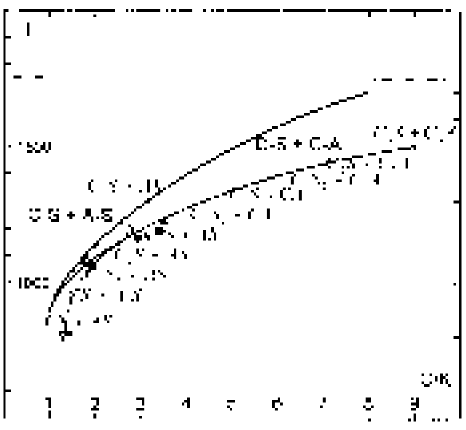

Fig 2. Dependence of the temperature of phosphogypsum-kaolin high-temperature interaction on a molar gypsum-kaolin ratio C/K. The dash line represents the breakdown temperature of pure gypsum. Numbers 1 – CAS_2 2; 3 – C_2AS; 4 – C_3AS_3

C/K=5:

$5CaSO_4 + Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = 2[2CaO \cdot SiO_2] + [CaO \cdot Al_2O_3] + 2H_2O + 5SO_2 + 2{,}5O_2$, $T_r > 1340$ K (20)

C/K = 6:

$6CaSO_4 + [Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = [3CaO \cdot 2SiO_2] + [3CaO \cdot Al_2O_3] + 2H_2O + 6SO_2 + 3O_2$, $T_r > 1410$ K (21)

C/K = 7:

$7CaSO_4 + [Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = 2[2CaO \cdot SiO_2] + [3CaO \cdot Al_2O_3] + 2H_2O + 7SO_2 + 3{,}5O_2$, $T_r > 1443$ K (22)

C/K = 9:

$9CaSO_4 + [Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O] = 2[3CaO \cdot SiO_2] + [3CaO \cdot Al_2O_3] + 2H_2O + 9SO_2 + 4{,}5O_2$, $T_r > 1513$ K (23)

4.5. Discussion of results and experiments

The calculated temperature T_r of phosphogypsum-kaolin interaction, K dependency on phosphogypsum and kaolin mole ratio C/K are given in Fig 2. As it can be seen the interaction temperature depends on the ratio C/K: the higher the ratio, i e the more CaO moles take part is the reaction, the higher is the process temperature. This law of nature can be expressed by two curves the first one of which represents C–S+A–S, and the second one – C–S+C–A systems. The three C–A–S system compounds anorthite CaS_2(1), helenite C_2AS (2, 3), grossularite C_3AS_3 (4) dots are close to the two curves. The system row is ended by the pure gypsum decomposition reaction (system 1). As we can see from the calculation results, C_2S is formed during the (4, 5, 12, 14) equation cases, at initial reaction temperatures > (1126–1443) K, i e > (853–1170) °C. The probability of C_2S formation process from phosphogypsum and kaolin mixtures heated up to 1200 °C can be arranged as follows: (4) > (5) > (12) > (14).

The following mixtures were heated: 1) phosphogypsum-kaolin (ratio 1 : 1; duration 5 h; temperatures 500, 700, 800, 900, 1000, 1200 °C), 2) phosphogypsum-kaolin (ratio 1 : 1; 2 : 1; 3 : 1; duration 30 h; temperature 1200 °C).

As can be seen from the X-ray diffraction pattern analysis of heated phosphogypsum and kaolin mixtures in the temperature range 500–1200 °C, the main compounds formed do not depend on the component proportions (1 : 1–3 : 1 interval) and on heating duration of 5 and 30 h. The main substances formed are:

1) incomplete calcination residue – anhydrite,

2) anorthite formed at higher than 816 K (543 °C)

temperatures according to reaction (7) (in Fig 2 its dot is in the lowest position),

3) cristobalite formed at higher than 1060 K (787 °C) according to reaction (8),

4) mullite formed at higher than 1430 K (1157 °C) temperatures,

5) C_2S formed at higher than 1126 K (853 °C) according to reaction (4), higher than 1220 K (947 °C) according to reaction (5) and higher than 1340 K (1067 °C) according to reaction (12).

Different composition of calcium silicates formed during a high-temperature reaction of phosphogypsum and kaolin depends on the temperature: the higher the temperature, the greater is the CaO/SiO_2 molar ratio of the formed silicate. The main reason of this is that with an increase in basic oxide CaO incoming mole number, as can be seen from the above presented calculations, the lower is the negative standard Gibbs energy change for a mole of CaO.

As a result of this, a higher temperature is needed for tricalcium silicate synthesis from gypsum and kaolin than for the case of dicalcium silicate (both compounds possess binding properties).

Calcium silicates, aluminates and alumosilicates (in all the 14 compounds) formation dependencies on gypsum and kaolin mixture heating temperature t_{rkc}, °C and the compound composition can be expressed by the following additive equation:

$$t_{rkc} = I_C \cdot C + I_A \cdot A + I_s \cdot S, \qquad (24)$$

where I_C, I_A, I_s – CaO, Al_2O_3 and SiO_2 increments; C, A, S – CaO, Al_2O_3 and SiO_2; % in the corresponding compound formula.

The solution of the 14 compound reaction equations according to the least square method allows us to obtain the following:

$$t_{rkc} = 8{,}14 \cdot C + 3{,}912 \cdot A + 2{,}849 \cdot S. \qquad (25)$$

The correlation coefficient of calculated values and values obtained from the above equation is 0,9346. This number F is a criterion showing that a corresponding hypothesis can be accepted at 5 % importance level and not rejected at 1 % level.

So the heating of phosphogypsum with kaolin can give us dicalcium and tricalcium silicate possessing binding properties.

The following compound peaks were registered by X-ray diffraction pattern analysis during heating phosphogypsum and kaolin mixtures at (500–1200) °C: phosphogypsum decomposition product – anhydrite; kaolinite decomposition products – quartz; cristobalite SiO_2 and mullite A_3S_2; anhydrite and kaolinite interaction products – anorthite CAS_2, helenite (melilite) C_2AS and belite C_2S; various admixtures present in the raw materials – feldspar and mica.

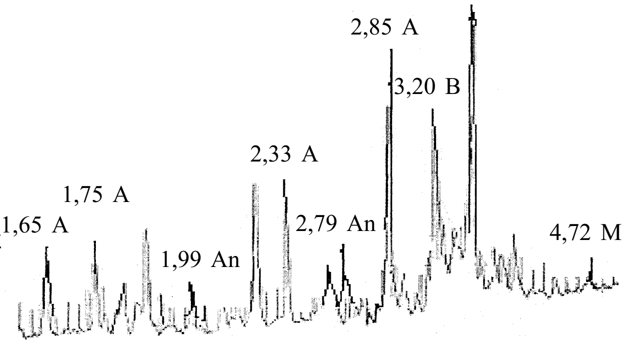

Fig 3. X-ray diffraction pattern of a phosphogypsum and kaolin mixture (2 : 1) heated at 1200 °C for 6 h. Note: An – anothite, A – anhydrite, B – belite, M – helenite (melilite)

A roentgenogram of a phosphogypsum and kaolin mixture (2 : 1), heated for 6 h at 1200 °C is given in Fig 3. Here we can see that anhydrite predominates, and belite is also present. However, for the formation of a more significant amount of alite, it seems that higher temperatures are required.

Specimens were formed from the obtained materials and their compressive strength was determined. The results were 7,2 MPa (in the case of ordinary structural gypsum the value reaches only 7 MPa, while for a high-quality structural gypsum – (15–20) MPa. So we can interpret the product results as that for a low-strength binding material. If we wish to obtain higher strengths, we need to heat the mixtures at higher temperatures.

5. Conclusions

1. Anhydrite binding materials containing CaO as binding activator can be obtained from natural gypsum, anhydrite or phosphogypsum and kaolin, by heating these raw materials at higher than 1200 °C temperatures. An exact heating temperature for obtaining an expected amount of CaO in the product can be calculated according to the given thermodynamic equation.

2. Various calcium silicates as well as aluminates, alumosilicates and calcium alumosilicates, including materials with binding properties possessing like C_2S and C_3S, can be obtained from a high-temperature (≥ 1200 °C) reaction of gypsum, anhydrite, phosphogypsum and kaolin interaction. The formation temperatures of these compounds can be calculated by using a linear additive equation. The obtained reaction products possess relatively low mechanical strength so the process should be conducted at higher than 1200 °C temperatures to obtain articles of a good quality.

3. The utilization of phosphogypsum could not only help to obtain structural materials from harmful production by-products, but also to decrease pollution arising from phosphogypsum waste into the atmosphere, wastewaters from leachates and soil by toxic hydrogen fluoride and other amounts of hazardous materials. The phosphogypsum utilization process can significantly improve the solution of environmental problems caused by the region's industry.

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AUKŠTATEMPERATŪRIS FOSFOGIPSO NUKENKSMINIMAS IR UTILIZAVIMAS

A. Kazragis

Santrauka

1. Anhidritinės rišamosios medžiagos, kurių sudėtyje yra rišimosi aktyviklio CaO, gali būti gaunamos iš gamtinio gipso, anhidrito arba fosfogipso ir kaolino, iškaitinant šias žaliavas aukštesnėse negu 1200 °C temperatūrose. Kaitinimo temperatūrą, būtiną norimam CaO kiekiui produkte gauti, galima apskaičiuoti, remiantis pateikiama termodinamine lygtimi.

2. Dėl aukštatemperatūrės (≥ 1200 °C) gipso, anhidrito arba fosfogipso ir kaolino sąveikos gali susidaryti kalcio silikatai bei aliuminatai, aliuminio silikatai ir kalcio aliumosilikatai, tarp jų ir medžiagos, tokios kaip C_2S bei C_3S, kurioms būdingos rišamosios savybės. Šių junginių susidarymo temperatūros gali būti apskaičiuotos, taikant linijinę adityvinę lygtį. Gautiems reakcijos produktams būdinga nedidelis mechaninis stiprumas, todėl gaminant dirbinius iš šių medžiagų, tikslinga, kad procesas vyktų aukštesnėse negu 1200 °C temperatūrose.

3. Fosfogipso utilizavimas ne tik padėtų iš žalingų gamybos atliekų gauti statybines medžiagas, bet ir iki minimumo sumažėtų iš fosfogipso terikonų į atmosferą, nutekamuosius vandenis bei gruntą patenkančių nuodingų fluoro vandenilio ir kitų kenksmingų medžiagų. Fosfogipso utilizavimo procesas padėtų spręsti apsaugos problemas gamybos rajone.

Raktažodžiai: nukenksminimas, utilizavimas, fosfogipsas, kaolinas, aukštatemperatūris apdeginimas, rišamosios medžiagos.

ВЫСОКОТЕМПЕРАТУРНОЕ ОБЕЗВРЕЖИВАНИЕ И УТИЛИЗАЦИЯ ФОСФОГИПСА

А. Казрагис

Резюме

Ангидритные вяжущие материалы, содержащие активатор схватывания CaO, могут быть получены путем совместного обжига смеси, состоящей из природного гипса, ангидрита или фосфогипса и каолина, при температурах ≥ 1200 °C. Температура, необходимая для получения определенной доли активатора в составе ангидрита, может быть определена с помощью предложенного термодинамического уравнения.

В результате высокотемпературного взаимодействия между гипсом, ангидритом или фосфогипсом и каолином могут образоваться силикаты, алюмосиликаты и алюмосиликаты кальция, в том числе и обладающие вяжущими свойствами C_2S и C_3S. Температуры образования этих соединений могут быть вычислены с помощью линейного аддитивного уравнения. Полученные продукты обжига обладают невысокой механической прочностью, поэтому при производстве изделий из таких материалов целесообразно проводить обжиг при температурах, превышающих 1200 °C.

Утилизация фосфогипса представляет собой возможность снизить до минимума концентрации попадающих из терриконов в атмосферу и грунтовые воды таких ядовитых веществ, как фтористый водород. Поэтому процесс утилизации фосфогипса должен положительно сказываться на процессе охраны окружающей среды в районе производства фосфогипса.

Ключевые слова: обезвреживание, утилизация, фосфогипс, каолин, высокотемпературный обжиг, вяжущие материалы.