THERMAL TREATMENT OF THE PHOSPHOGYPSUM BRIQUETTES IN WATER VAPOUR UNDER ELEVATED PRESSURE

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Wet process of impurities neutralization or their removal from phosphogypsum considerably increases the cost price of the product. The principal possibilities for the thermal treatment of dihydrate phosphogypsum into the gypsum binder by escaping wet processing are discussed in the paper. The pressure of saturated water vapour is not a sufficient condition initiating a complete neutralization reaction between the acidic impurities of phosphogypsum and the neutralization admixture or determining the growth of hemihydrate gypsum crystals. Under such condition, the transfer of the materials between particles does not take place. To achieve it, the cavities between the particles in the phosphogypsum briquette should be filled with water. Under this condition, the most reliable admixtures neutralizating the acidic impurities are ground carbonate solids (e.g. chalk, limestone, dolomite).

INTRODUCTION

A successful utilization of phosphogypsum in the production of building materials is impeded by the acidic impurities found in its composition that considerably worsens the properties of the products [1,2]. Actually, in all technologies applied for the processing of phosphogypsum into the gypsum binder wet processing are used for the elimination [3,4] or neutralization [5,6] of impurities. In such cases the great amount of water must be eliminated by evaporation. It considerably increases the energetic expenditure, and the obtained product turns to be incompetitive to the plaster of Paris produced from natural gypsum stone. On the other hand, the technology for the production of the gypsum binder by processing flinders of gypsum stone in the environment of the saturated water vapour of raised pressure in autoclave allows for obtaining the gypsum binder of high quality [7]. This method was used to obtain an extremely strong gypsum binder from the mixture of ground gypsum stone and the admixture that controls crystallization of hemihydrate gypsum [8]. The mixture with 1-2 % of water was pressed under 12-18 MPa pressure. It has concluded that the thickening of the pressed bricks should not be lower than 1780 kg/m^3. The neutralization process of phosphogypsum impurities was carried out under normal pressure in water environment or in the unsaturated water vapour [9]. It was determined that the initial product of the interaction between acidic orthophosphates and the chalk was little soluble calcium hydrogenorthophosphates ($CaHPO_4 \cdot 2H_2O$) that very slowly react with the neutralizer thus forming the least soluble combinations - calcium orthophosphates belonging to the group of hydroxylapatites $Ca_3(PO_4)_2 \cdot nH_2O$ and $Ca_5(PO_4)_3OH \cdot mH_2O$. The direction of the reaction between soluble phosphates and lime was determinated by the fluxes of soluble materials: when the dissolved lime dominated in the environment (it was alkaline), the direct formation of calcium orthophosphates belonging to the group of hydroxylapatites took place; when the soluble phosphates dominate (the environment was acidic), the formation of the final product took place through the intermediate phase - $CaHPO_4 \cdot 2H_2O$.

The paper aim is the determining of the principal possibilities for the processing of dihydrate phosphogypsum into the gypsum binder by escaping wet processing. The research is based on:

1) an analysis of the neutralization of the acidic impurities found in phosphogypsum in the natural and modelled systems of the environment of saturated water vapour of raised pressure;
2) the investigation of phosphogypsum dehydration and hemihydrate gypsum crystallization in this environment;
3) the determination of the properties of the produced binder.

EXPERIMENTAL

Phosphogypsum (calcium sulphate dihydrate - by-product of Kola apatite) dug out in Kedainiai terricones at the depth of 0.3-0.5 m was used for the experiments.

The loss on ignition at 400°C was 34.7 wt.%, total P_2O_5 made 1.38 wt.%, water soluble P_2O_5 was 0.39 wt.%, total F made 0.34 wt.%, water soluble F was 0.04 wt.%.

For the neutralization of the acidic impurities in phosphogypsum, three types of admixtures were used: 1) ground quicklime from Akmene containing 71 wt.% CaO + MgO; 2) reagent chalk and 3) ground dolomite from Petrasiunai whose specific surface by Blain was 146 m^2/kg. Other materials were of chemical purity.

The experiments were carried out on the pilot phosphogypsum processing line where about 7 kg of the gypsum binder may be produced at once. The line consists of the mixer, the rammer, the press P-50 (capacity - 500 kN), the steam generator with the steam super heater, the horizontal autoclave (volume - 30 l) and the ball mill. The steam feed system of the tube networks and valves allowed for the testing of different kinds of phosphogypsum thermal processing in the autoclave. Special thermometers and monometers were fitted in the steam generator and in the autoclave.

Phosphogypsum (10 kg), including the mixed neutralizating admixture or without it, was thickened by ramming and pressing in to 4 briquettes or poured loose into the perforated nozzle and put into the autoclave. The steam produced in the steam generator was used for the heating of the autoclave from outside. Its temperature was not higher than 210°C in order to avoid the formation of anhydrite. The environment of the saturated water vapour in the autoclave was affected by evaporation of moisture from phosphogypsum. After phosphogypsum dehydration the speed of the emission of the saturated water vapour from the autoclave was controlled by not allowing the temperature in the autoclave to fall below 120°C. When moisture was evaporated, the material was taken off from the autoclave, then cooled and ground. After the thermal treatment the cooled material was ground in the ball mill for 30 min.

The model mixtures from $Ca(H_2PO_4)_2 \cdot H_2O$ and $CaHPO_4 \cdot 2H_2O$ with the powder of lime, chalk, dolomite or chalk-stone were placed to the autoclave with the phosphogypsum briquettes. The brusite ($CaHPO_4 \cdot 2H_2O$) was synthesized from stoichiometric amount of the reagent chalk and orthophosphorus acid solution. After the thermal treatment the X-ray analysis of the obtained product was carried out.

The fineness of the ground material was determined by applying air permeability with the use of the PSH-4.

pH of the materials was measured with an universal pH-meter by mixing the material in distilled water at the ration 1:3.

The microscopic analysis was carried out with the use of the optical microscope MIN-8 and scanning electronic microscope JSM-5000 (SEM).

X-ray phase analysis was performed using a DRON-6 diffractmeter with CuKα radiation and Ni-filter. Concentration of the alkali in the solution was determined with flame photometer ATS 200S.

The water and gypsum ratio (W/G) of gypsum binder was determined using Suttard Viscosimeter, setting time - using knife method and compressive strength - using press P-5 (bias 0.1 kN) according to [10].

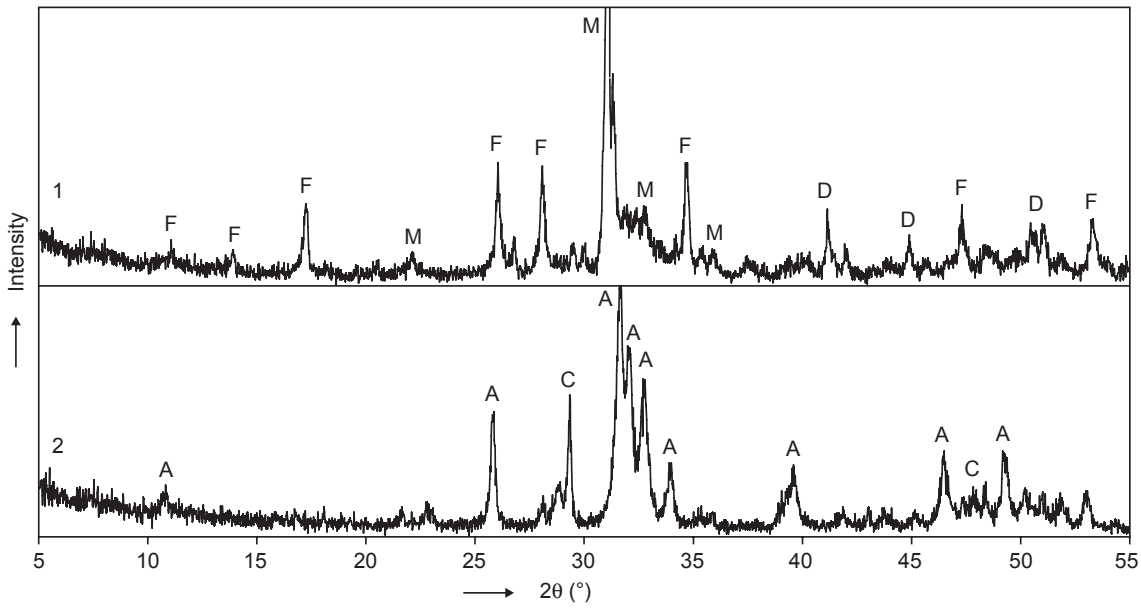

Figure 1. X-ray diffraction patterns of the reaction products of $CaHPO_4 \cdot 2H_2O$ with dolomite (1) and chalk (2) at 0.8 MPa pressure (cavities between the particles were filled with water). Notation: C - $CaCO_3$; D - $CaMg(CO_3)_2$; A - $Ca_5(PO_4)_3OH$; M - $Ca_4Mg_5(PO_4)_6$; F - $Ca_7Mg_2P_6O_{24}$.

RESULTS AND DISCUSSION

When the external part of the autoclave was heated under constant 210°C temperature, the diagram of pressure in the autoclave was very similar to the diagram of temperature in the case of gypsum thermal treatment in the boiler: 2 h rising to 0.2 MPa, the horizontal platform at the 0.2 MPa pressure and 4 h rising to 0.8 MPa.

The experiment of the gypsum binder production when the mixture of phosphogypsum of natural moisture and the neutralizating admixture was poured into nozzle and put into the autoclave did not bring positive results. Water and gypsum ratio (W/G) of such material was 1.1. After the grinding the W/G of the obtained gypsum binder remained high (0.67-0.75). From the produced binder paste, CO_2 gas was detached when the carbonate materials were used as neutralizating admixtures. It shows that the reaction of the acidic impurities with the carbonate neutralizing admixtures was not finished during the technological processing and continued when the binder was mixed with water.

It appeared that during the entire period of phospho-gypsum dehydration and drying the loose mixtures of the reacting materials in the environment of the saturated water vapour of heightened pressure did not react with each other. A different situation was observed in the X-ray diffraction pattern when the cavities between the particles were filled with water. In this case, during the period of the thermal treatment of phosphogypsum the reaction was complete - only the peaks of high base phosphates are observed (Figure 1).

The determined regularity was further applied for the thermal treatment of phosphogypsum. Before the thermal treatment the mixture of dihydrate phosphogypsum of natural moisture with the neutralizating admixture or without it was thickened to allow the moisture inside phosphogypsum fully fill the cavities between the particles (until water emission took place). For this reason, the mixture was rammed or pressed by using the power of the determined strength. The produced phosphogypsum briquettes were put into the autoclave.

The main data of the preparation, thermal treatment and grinding of dehydrate phosphogypsum and of the properties of the obtained products are presented in Table 1.

The microscopic analysis of thermally treated phosphogypsum demonstrated that, irrespective of the pressure of the saturated water vapour, the crystals of hemihydrate gypsum were fine and were found in the carcasses of the initial of crystals of the dihydrate phosphogypsum (Figure 2).

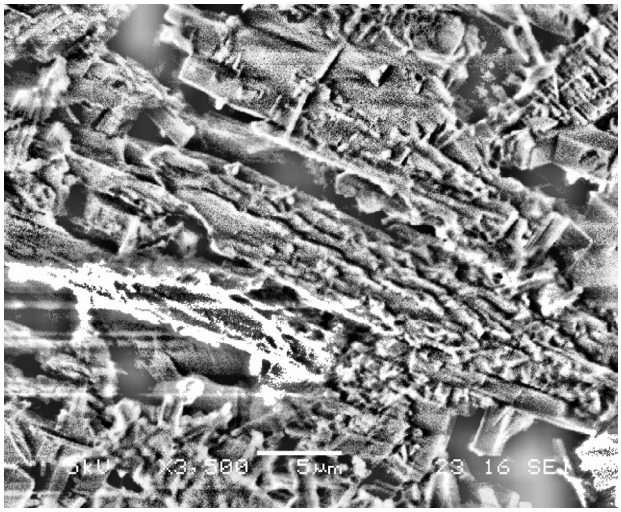

Figure 2. Dehydrated phosphogypsum after thermal processing, wherein the cavities between the particles have been filled by saturated water vapour.

Table 1. Parameters for the preparation and processing of the phosphogypsum and indications of the obtained product.

Admixture and preparation of the briquettes	Briquet density (kg/m³)	Condition of dehydration	Properties of the binder				
			Ignition (%)	*S* (m²/kg)	pH	V/G	Setting time (min)
2 % of dolomite, without thickening	-	The steam was supplied	1.75	480	5.8	0.72	15
Without admixtures, rammed	1180	to outside of the autoclave	5.86	416	5.1	0.45	12
1 % of dolomite, rammed	1190		5.59	461	7.1	0.44	10
2 % of dolomite, rammed	1190		6.53	444	7.6	0.43	9
0.5 % of quicklime, rammed	1200		5.91	442	7.8	0.43	14
1 % of quicklime, rammed	1200		5.18	440	11.9	0.44	25
2 % of dolomite, pressed up to 21 MPa	1880		3.64	436	7.5	0.42	11
2 % of dolomite, pressed up to 57 MPa	1960		5.79	419	7.5	0.41	10
2 % of dolomite, without thickening	-	The steam was supplied to intside of the autoclave	5.20	451	7.8	0.44	12
1 % of dolomite, rammed	1070		5.58	427	7.0	0.42	11
2 % of dolomite, rammed	1080		5.91	431	7.9	0.41	11
0.5 % of quicklime, rammed	1060		5.47	443	7.2	0.43	12

If the cavities between the crystals of the dihydrate phosphogypsum were filled with water before the thermal treatment, the crystals of hemihydrate phosphogypsum grew large and were formed as detached from the carcasses of admixtures (Figure 3).

The impact of the density of the briquettes made of the mixture of phosphogypsum and the neutralizating admixture on the properties of the obtained product before thermal treatment is presented in Figure 4.

As the given data shows, the density of the thickened briquettes has no influence on the obtained binder's compressive strength: most important is to have the cavities between the particles filled with water. Such a requirement is not fulfilled in the case of loose mixture of phosphogypsum and the neutralizating admixture.

The gypsum binder's compressive strength after 2 h of hardening when the binder was produced in the autoclave with external heating by the dehydration of rammed phosphogypsum with the dolomite admixture or without it is presented in Figure 5.

Although the compressive strength of the obtained gypsum binders is similar, nevertheless, the medium of their paste (pH) differs considerably (see Table 1): when including dolomite, it is alkaline. Without admixtures it is acidic, i.e. the latter composition cannot be used in the mixtures with cement or lime. In the discussed case, the residual acidic admixtures will react with lime and thus produce the high base calcium orthophosphates of the hydroxylapatite group, which will consequently prevent the hardening of the mixture.

When lime is used for the neutralization of the acidic admixtures in rammed phosphogypsum, their excess slows down the initial hardening of the product.

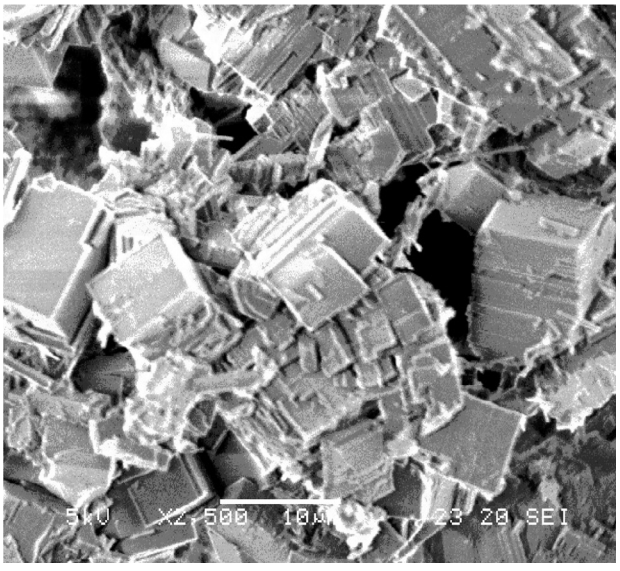

Figure 3. Dehydrated phosphogypsum after thermal processing, wherein the cavities between the particles have been filled by water.

The gypsum binder produced with the use of dolomite as a neutralizating admixture demonstrates the properties typical of the plaster of Paris, i.e. the highest strength was reached after 2 h hardening. Contrary, the initial compressive strength of the samples including lime as a neutralizating admixture was rather low. In the discussed type of binder, there was the excess of the neutralizating admixture (i.e. lime) and thus demonstrates pH suspension of the gypsum binder - 11.9 (see Table 1). The slowing down effect of lime on the plaster of Paris was discovered long ago, therefore, in the case of lime used as a neutralizating admixture, it is urgent to examine the exact composition of the acidic impurities as well as their amount in phosphogypsum in order to escape their excess and thus achieve the complete binding of the least soluble combinations.

It should be pointed out that the excess of the carbonate neutralizating admixtures has no impact on the properties of the gypsum binders.

Input of the admixture (sodium alkylsulfobensol) that controls crystallization of hemihydrate gypsum in

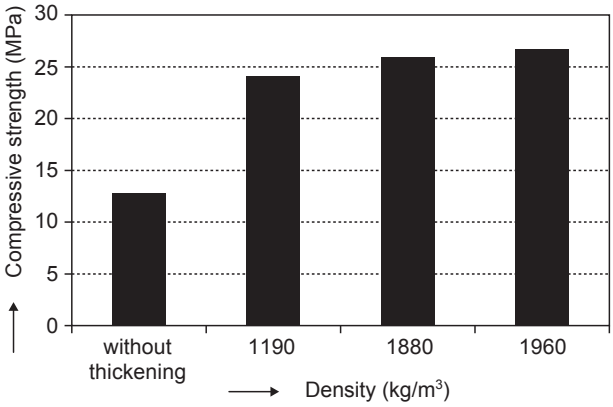

Figure 4. Influence of briquettes density (phosphogypsum + 2 % dolomite) on the compressive strength of the gypsum binder.

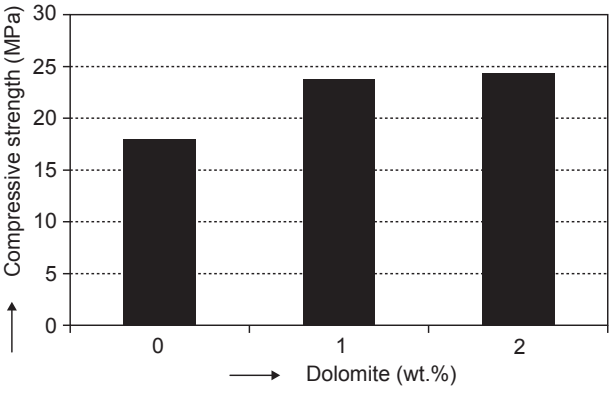

Figure 5. Influence of dolomite quantity in phosphogypsum briquettes (density 1200 kg/m^3) on compressive strength of the gypsum binder.

the briquettes from mixture of the phosphogypsum with the neutralizating admixture has not raised strength of the gypsum binder.

If the autoclave is heated by feeding the steam to inside the cavities between the particles of phosphogypsum may be did not fill with water. In this case the cavities filled up condensate. The properties of produced gypsum binder (see Table 1) did not differ from the above-discribed (when the cavities between the particles were filled with water). The alkali was determinded in the condensate from autoclave (Figure 6).

The water vapour from the autoclave have not alkali and may be used for recycling.

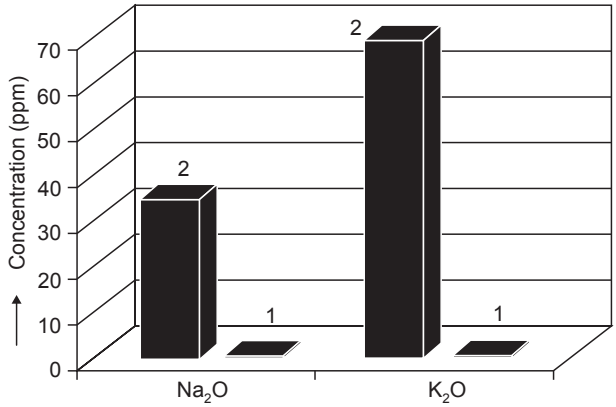

Figure 6. Concentration of alkali in the steam (1) and in the condensate (2) on the outlet of the autoclave.

CONCLUSION

1. The pressure of the saturated water vapour is not a sufficient condition causing a complete neutralization reaction between the acidic impurities of phosphogypsum and the neutralizating admixture and determining the growth of hemihydrate gypsum crystals. Under such condition, the transfer of the materials between the particles does not take place. To achieve it, the cavities between the particles should be filled with water.
2. The cavities between the particles may be filled with water by thickening of the mixture of phosphogypsum with natural moisture and the neutralizating admixture until water emission is obtained or feeding steam to autoclave.
3. The most reliable admixtures neutralizating of the acidic impurities are ground carbonate solids (e.g. limestone, dolomite, chalk) that during phosphogypsum dehydration bind the impurities of fluorine and phosphate into the least soluble combinations (i.e. calcium fluoride and calcium orthophosphates of hydroxylapatite group). Their excess does not worsen the properties of the obtained gypsum binder.
4. The thickening of phosphogypsum determines only the energetic expenditure - the more thickened the material is, the smaller the cavities between their particles that should be filled with water which, in its turn, should be evaporated after dehydration of phosphogypsum.

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TEPELNÉ ZPRACOVÁNÍ FOSFOSÁDROVCOVÝCH BRIKET VE VODNÍ PÁŘE ZA ZVÝŠENÉHO TLAKU

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Mokrý proces neutralizace příměsí ve fosfosádrovci nebo jejich odstranění výrazně zvyšuje výrobní cenu produktu. V práci jsou diskutovány hlavní možnosti tepelného zpracování dihydrátu fosfosádrovce na sádrové pojivo při opuštění mokré cesty. Tlak nasycené vodní páry není podmínkou postačující pro inicializaci úplné neutralizační reakce mezi kyselými nečistotami ve fosfosádrovci a neutralizační směsí ani neurčuje růst krystalů hemihydrátu sádry. Za takových podmínek nedochází k přesunu materiálů mezi částicemi. Abychom toho dosáhli, je třeba vyplnit mezery mezi částicemi ve fosfosádrovcové briketě vodou. Za tohoto stavu jsou nejspolehlivější směsí neutralizující kyselé příměsi drcené pevné uhličitany (např. křída, vápenec, dolomit).