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Dehydration of Phosphogypsum and Neutralization of It's Impurities in the Steam of Raised Pressure

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Wet process of impurities neutralization or their removal from phosphogypsum considerably increases the cost price of the product. Alternative principal possibilities for the treatment of dihydrate phosphogypsum into the gypsum binder by escaping wet processing are discussed in the paper. The pressure of saturated water steam is not a sufficient condition initiating a complete neutralization reaction between the acidic impurities of phosphogypsum and the neutralization admixture and 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 should be filled with water. The offered case is based on the thickening of the mixture of natural moisture phosphogypsum and the ground carbonate solid until water emission is obtained. The prepared briquettes process in the autoclave.

Keywords: phosphogypsum, impurities, neutralization, autoclave.

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 – 3]. Actually, in all technologies applied for the processing of phosphogypsum into the gypsum, binder wet processing are used for the elimination [4, 5] or neutralization [6, 7] 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. The authors have made an attempt at describing an alternative to wet processing. The technology for the production of the gypsum binder by processing flinders of gypsum stone in the environment of the saturated water steam of raised pressure in vertical (damphers) [8] or horizontal [10] autoclaves allows for obtaining the gypsum binder of high quality. L. J. Klykova used mentioned method to obtain an extremely strong gypsum binder from the mixture of ground gypsum stone and the admixture that controls crystallization of hemihydrate gypsum. The mixture with 1 % – 2 % of water was pressed under 12 MPa – 18 MPa pressure. Klykova has concluded that the thickening of the pressed bricks should not be lower than 1780 kg/m^3. However, no data regarding the employment of the discussed method for the processing of phosphogypsum into the gypsum binder was found in the works of the mentioned author or in any other scientific sources.

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 water steam of raised pressure; 2 – the investigation of phosphogypsum dehydration and hemihydrate gypsum crystallization in the environment of the steam of raised pressure; 3 – the determination of the properties of the produced binder.

MATERIALS AND METHODS

Dehydrate phosphogypsum dug out in Kėdainiai terricones at the depth of 0.3 m – 0.5 m was used for the experiments whose loss on ignition at 400 °C was 35.4 %, total P_2O_5 made 1.45 %, water soluble was P_2O_5 0.63 %, total F made 0.35 %, water soluble F was 0.05 %.

For the neutralization of the acidic impurities in phosphogypsum, three types of admixtures were used: 1 – ground quicklime from Akmenė in witch $(CaO + MgO)_{act}$ made 71 %; 2 – reagent chalk and 3 – ground dolomite from Petrašiūnai whose specific surface by Blain was 146 m^2/kg. Other materials were clean or chemically clean.

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 (bias 1 kN), the steam generator (up to 220 °C of temperature), the steam super heater (up to 270 °C of temperature), the horizontal autoclave, the dryer 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 the autoclave for the observation and control of the processing and their indications were registered by self-recording instruments.

Phosphogypsum (10 kg), including the mixed neutralizating admixture or without it, was thickened by ramming and pressing or poured loose into the perforated nozzle and put into the autoclave. Thickening was carried out until water was separated. After the thermal treatment the cooled material was ground in the ball mill for 30 min.

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

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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. X-ray phase analysis was performed using a DRON-6 diffractmeter with CuK_α radiation and Ni-filter.

Water and gypsum ratio (W/G) was determined using Suttard Viscosimeter, setting time – using a Vicat Needle Apparatus and compessive strength – using press P-10 (bias 0.2 kN) acording to [11].

The kinetics of hardening was determined by keeping the samples under the hermetic conditions that prevented moisture from evaporation.

RESULTS AND DISCUSSION

The technological choise 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 which the steam of 0.2 MPa – 1.4 MPa pressure and 130 °C – 190 °C temperature (used for heating and dehydration of the equipment and the material) did not bring positive results. The moisture of the taken out dehydrated phosphogypsum was high because during heating by steam some part of the condensate did not run down but remained among the particles of phosphogypsum. During steam emission only some part of the condensate is evaporated, therefore a considerable amount of it should be dried in the dryer. When it is taken out from autoclave, the material gets cooled and is partially hydrated. The microscopic analysis demonstrated that after such treatment the hemihydrate phosphogypsum crystals became very fine and were formed within the carcass of the dehydrate phosphogypsum admixtures. Water and gypsum ratio (W/G) of such material was ≥1.1. After the grinding the W/G the obtained gypsum binder remained high (0.67 – 0.75). The setting time of the binder is long and it not complete in 2 hours. 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. The supply of the steam superheated up to 270 °C into the autoclave partially improved the drying; yet, the properties of the binder were improved rather inconsiderably.

In further experiments 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 steam in the autoclave was affected by evaporation of moisture from phosphogypsum. After phosphogypsum dehydration the speed of the emission of the saturated water steam from the autoclave was controlled by not allowing the temperature in the autoclave to fall below 150 °C. When moisture was evaporated, the material was taken off from the autoclave, then cooled and ground.

In case of heating from outside, when the perforated nozzle filled with the mixture of phosphogypsum and the neutralizating admixture was put into the autoclave, the properties of produced gypsum binder did not differ from the above-described mixture, (i.e. when the steam was supplied into the autoclave). It should be stressed that after two hours the setting time of the prepared gypsum binder paste had not been finished.

In order to investigate the mentioned reasons, the process of the neutralization of impurities was analysed on the basis of the discussed modelling system. Similar explorations, only under normal pressure in water environment or in the unsaturated water steam were carried out [6]. It was determined that the initial products of the interactions between acidic orthophosphates and the carbonate neutralizating admixtures were little soluble calcium or magnesium hydro orthophosphates that very slowly react with the neutralizer thus forming the least soluble combinations – calcium or magnesium phosphates belonging to the group of hydroxylapatites. 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 – $CaHPO_4 \cdot 2H_2O$.

To investigate the process of the mentioned reaction in the environment of the saturated water steam of raised pressure, the brusite ($CaHPO_4 \cdot 2H_2O$) was synthesized from the stoichiometric amount of reagent chalk and orthophosphorus acid solutions. The synthesized brusite was mixed with the neutralizating admixture and put into the autoclave with phosphogypsum processed in it. Dolomite, chalk and lime were used as neutralizating admixtures. After the thermal treatment the X-ray analysis of the obtained product was carried out. It appeared that during the entire period of phosphogypsum dehydration

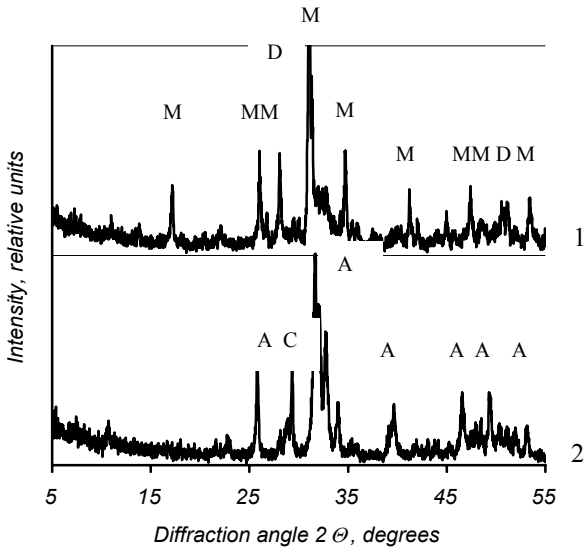

Fig. 1. X-ray diffraction patterns of the products of the reactions of dolomite and chalk with $CaHPO_4 \cdot 2H_2O$ in the environment of the saturated water steam of heightened pressure (cavities between the particles were filled with water): 1 – dolomite; 2 – chalk. Notations: C – $CaCO_3$; D – $CaMg(CO_3)_2$; A – $Ca_5(PO_4)_3OH$; M – $Ca_7Mg_2(PO_4)_6$

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

No	Admixtures and preparation	Density, kg/m^3	Autoclave, at finish			After grinding		
			after heating		drying, °C	ignition, %	*S*, m^2/kg	pH
			t, °C	*p*, MPa				
1	2 % of dolomite, without thickening	–	195	0.95	194	1.75	430	7.8
2	Without admixtures, rammed	1180	190	0.83	194	5.86	416	5.1
3	1 % of dolomite, rammed	1190	188	0.8	193	5.59	461	7.1
4	2 % of dolomite, rammed	1190	188	0.74	194	6.53	444	7.6
5	0.5 % of quicklime, rammed	1200	185	0,68	193	5.91	442	11.8
6	1 % of quicklime and 1 % of $SiO_{2act.}$, rammed	1200	189	0.74	194	5.18	440	10.9
7	2 % of dolomite, pressed up to 21 MPa	1880	163	0.4	188	3.64	436	7.5
8	2 % of dolomite, pressed up to 57 MPa	1960	176	0.4	182	5.79	419	7.5

and drying the loose mixtures of the reacting materials in the environment of the saturated water steam of heightened pressure did not react with each other. A different situation was observed in the X-ray diffraction patterns when the cavities between the particles were filled with water (Fig. 1).

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.

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 bricks were put into the autoclave.

When the external part of the autoclave was heated under constant 210 °C temperature, the diagram of pressure kinetic in the autoclave was very similar to the temperature kinetic diagram in the case of gypsum thermal treatment in the boiler (Fig. 2).

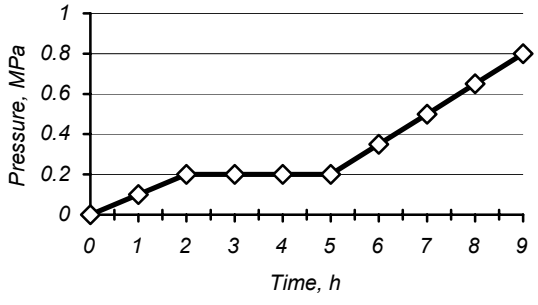

Fig. 2. Diagram of pressure kinetic in the autoclave (heated from outside) during phosphogypsum dehydration

The main data of the preparation, thermal treatment and grinding of dehydrate phosphogypsum and of the properties of the obtained products are presented in Table1.

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 Fig. 3. 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.

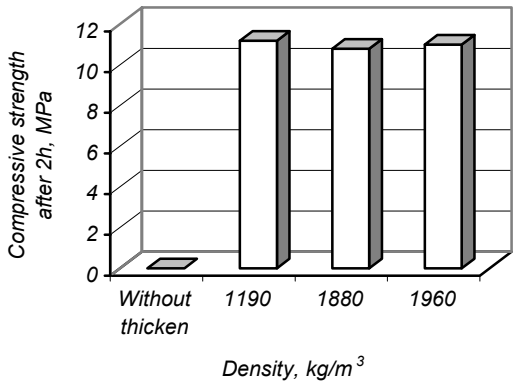

Fig. 3. The impact of the thickening of briquettes made of the mixture of phosphogypsum and 2 % of dolomite before thermal treatment on the compressive strength after 2 h hardening of the gypsum binder

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 Fig. 4.

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 (Fig. 5).

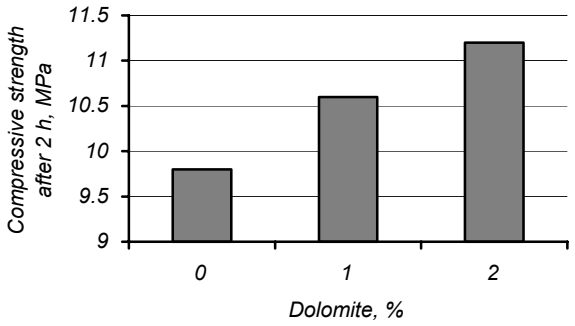

Fig. 4. The impact of dolomite amount in the thickened briquettes made from the mixture of phosphogypsum and neutralizating admixture before thermal treatment on the gypsum binder's compressive strength after 2 h hardening

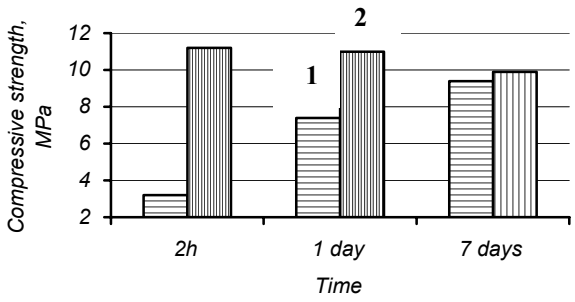

Fig. 5. The impact of the neutralizating admixture on the gypsum binder's kinetic of hardening under moisturous conditions: 1 – 2 % of dolomite; 2 – 0.5 % of quicklime

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 which, when the samples were kept under the moisturous conditions, started getting lower. Contrary, the initial compressive strength of the samples including lime as a neutralizating admixture was rather low; however, when the samples were kept under the moisturous conditions, their compressive strength was growing. 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 – 11.8 (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.

The microscopic analysis of thermally treated phosphogypsum demonstrated that, irrespective of the pressure of the saturated water steam, the crystals of hemihydrate gypsum were very fine and were found in the carcasses of the initial of crystals of the dihydrate phosphogypsum. 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.

CONCLUSIONS

1. The gypsum binder may be produced of the dihydrate phosphogypsum by escaping wet processing; the case offered in the paper is based on the thickening of the mixture of phosphogypsum with natural moisture and the neutralizating admixture until water emission is obtained.

2. The pressure of the saturated water steam 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.

3. Under mentioned conditions, the most reliable admixtures neutralizating the acidic impurities are ground carbonate solids (e.g. limestone, dolomite, opoca) 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. In the discussed case, the thickening of phospho-gypsum 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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