INFLUENCE OF DEHYDRATION METHOD ON THE MORPHOLOGY OF HEMIHYDRATE GYPSUM CRYSTALS

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Gypsum raw material (reagent gypsum, phosphogypsum and processed phosphogypsum) was dehydrated by dry method (i.e. in dry air environmental) and wet method (i.e. saturated water vapour environment) using microwaves. Influence of dehydration method on hemihydrate gypsum, hemihydrate phosphogypsum and processed hemihydrate phosphogypsum crystal morphology was researched. Gypsum raw material dehydration in dry air environment using microwaves does not significantly influence the morphology of hemihydrate gypsum, hemihydrate phosphogypsum or processed hemihydrate phosphogypsum crystals. Meanwhile, when raw material is dehydrated in the saturated water vapour environment using microwaves, the produced product crystals are smaller comparing to crystals of products dehydrated without microwaves. Therefore, it may be stated that using microwaves for gypsum raw material dehydration has no positive effect on the morphology of the obtained product crystals.

Keywords: gypsum, phosphogypsum, dehydration, microwaves, crystals.

1. Introduction

Gypsum binding materials (BM) are widely used in building products industry. Hemihydrate gypsum BM is produced using natural gypsum or industrial waste containing calcium sulphate, such as phosphogypsum [1-3]. Phosphogypsum contains some amounts of impurities, such as phosphoric acid, calcium phosphates, sodium silicofluoride and others. Phosphate impurities have a negative effect on setting and hardening of gypsum binding materials. In order to reduce this effect, phosphate impurities are neutralized in various ways [2, 4-7]. Hemihydrate gypsum is obtained by dehydrating gypsum raw material in dry air (e.g., driers, kettle) or saturated water vapour environment (e.g., autoclave). Morphology and physical-mechanical properties of the obtained binding material depend on raw material dehydration method [1, 8]. Today gypsum is dehydrated using microwaves [9-14]. However, there is a lack of data what influence microwaves have on the morphology of the obtained hemihydrate gypsum crystals. The aim of this research is to determine how microwaves used for the gypsum raw material dehydration influence morphology of the obtained hemihydrate gypsum crystals.

2. Experimental
2.1. Materials

Reagent gypsum $CaSO_4 \cdot 2H_2O$ (purity 99.97%). pH is 7.8. Specific surface area S of reagent gypsum is 550 m^2/kg.

Dihydrate phosphogypsum is the waste generated in JSC Lifosa from the production of phosphoric acid using Kirovsk apatite. Phosphogypsum was taken from the waste mound and dried in room temperature. Phosphogypsum contains 95% of dihydrate gypsum $CaSO_4 \cdot 2H_2O$ and the rest is various impurities. Impurities contain 1.5% of phosphates (P_2O_{5total}), including 0.75% of water soluble phosphates ($P_2O_{5w.s.}$). Chemical composition is given in Table 1. pH is 3.1. Specific surface area S of phosphogypsum is 140 m^2/kg. X-ray diffraction pattern is given in Figure 1.

Processed phosphogypsum is the phosphogypsum processed by a rotating magnetic field. After treatment phosphogypsum contains 97.5% of dihydrate gypsum $CaSO_4 \cdot 2H_2O$ and the rest is impurities, including $P_2O_{5total} - 0.5\%$, $P_2O_{5w.s.} - 0.1\%$. Chemical composition is given in Table 1. pH is 5.7, specific surface area $S - 250$ m^2/kg.

Maleic anhydride $C_4H_2O_3$ (purity 99.9%).

2.2. Methods

The processed phosphogypsum is obtained by exposing the dihydrate phosphogypsum suspension (water/gypsum ratio $W/G = 1$) to the rotating magnetic field. Phosphogypsum particles were broken down and soluble phosphate impurities inside crystals were transferred to liquid phase. The chemical analysis confirms that the amount of phosphates was reduced in the processed phosphogypsum. After treatment the

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Table 1

Chemical composition of phosphogypsum and processed phosphogypsum

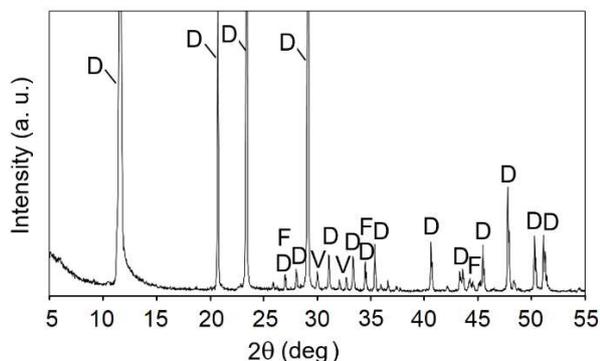|	Constituents, wt. %										
	CaO	MgO	SO$_3$	P$_2$O$_5$	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	K$_2$O	F	Ignition loss
Phosphogypsum	32.4	0.03	44.52	1.5	0.5	0.46	0.25	0.37	0.04	0.03	19.88
Processed phosphogypsum	32.69	0.03	45.39	0.5	0.35	0.27	0.16	0.16	0.02	0.02	20.41

Fig. 1 – X-ray diffraction patterns of phosphogypsum. *Indexes:* D – dihydrate gypsum CaSO$_4$·2H$_2$O, V – whitlockite Ca$_3$(PO$_4$)$_2$, F – fluorapatite Ca$_5$(PO$_4$)$_3$F.

solid phase (sediments) was separated from the liquid phase and dried.

Gypsum materials were dehydrated in dry air or saturated water vapour environment. Gypsum dehydration in the dry air environment was carried out as follows: *a*) 90 minutes in the convection drier at 140 °C temperature; *b*) 90 minutes in the household SAMSUNG microwave oven at capacity 450 W. Gypsum dehydration in the saturated vapour environment was carried out as follows: *a*) in the autoclave "Parr Instruments 4765"; *b*) in the microwave reactor "Monowave 300". The suspension of water/solid ratio W/S = 3 was prepared. Crystallization was controlled using maleic anhydride (0.2% of the used dry material (gypsum) amount). Dehydration process was carried out by mixing the suspension at temperature 135 °C. The duration of isothermal curing was 3 hours. After dehydration, the suspension was filtrated through Buchner filter and the obtained material was dried for 24 hours at temperature 100±2 °C.

Chemical composition was determined according to the European Standard EN 196-2-2005. The amount of P_2O_5 was determined using the yellow phosphor-vanadium-molybdenum complex.

The X-ray diffraction analysis (XRD) was carried out with a DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu K$_\alpha$ radiation and graphite monochromator, operating at 30 kV voltage and 20 mA emission current. The step-scan covered the angular range 5–60° (2θ) in steps of 2θ = 0.02°.

The hydration water in gypsum and phosphogypsum (Ignition loss, %) was calculated after heating the material at 400 °C temperature.

The pH measurements of water suspensions were conducted by pH-meter FE20, when the ratio of water (W) and solid material (S) W/S – 10.

The specific surface area *S* was determined by the Blaine´s method according to the European Standard EN 196-6-2005.

The particle size distribution was determined by a laser particle size analyzer (CILAS 1090 LD) in intervals from 0.05 to 500 μm.

Scanning electron microscopy (SEM) was performed with FEI QUANTA 200 FEG using an accelerating voltage of 20 kV at working distance of 10 mm.

Calorimetric analysis was performed using a TAM AIR III isothermal calorimeter. The temperature of experiment was 25±0.1 °C. The water to hemihydrate gypsum ratio was 0.5. The heat evolution rate was measured for 24 h.

3. Results and discussion
3.1. Raw material SEM analysis and granulometric composition
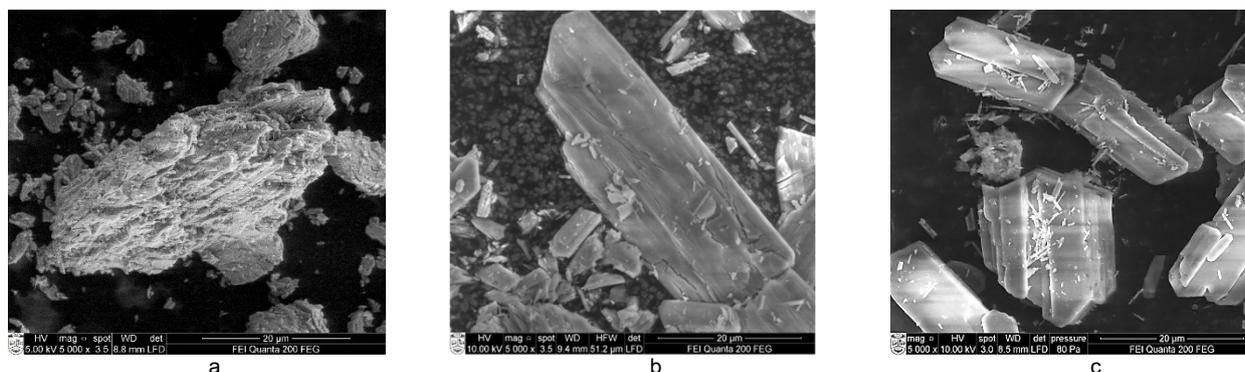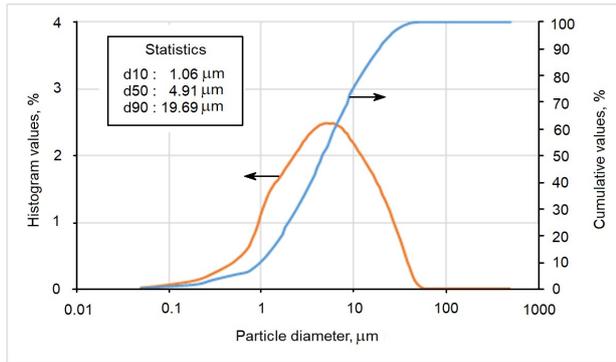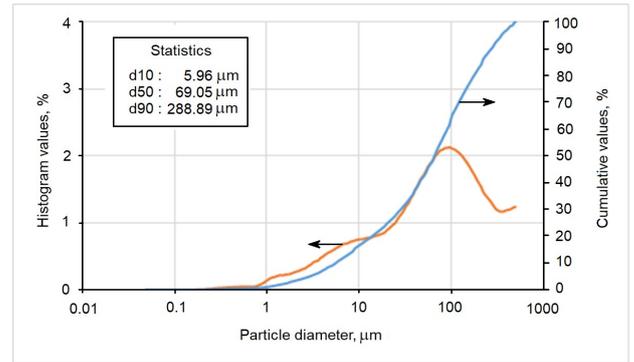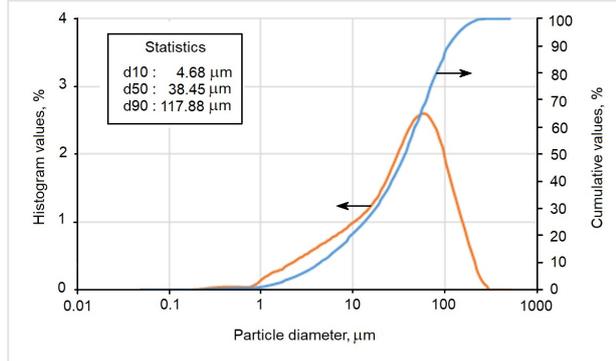
Raw material SEM analysis (Fig. 2) shows

Fig. 2 - SEM of reagent gypsum (a), phosphogypsum (b) and processed phosphogypsum (c).

a

b

c

Fig. 3 - Particles size distribution of reagent gypsum (a), phosphogypsum (b) and processed phosphogypsum (c).

that crystal shapes of reagent gypsum, phosphogypsum, and processed phosphogypsum are different. The shape of reagent gypsum crystals is irregular, phosphogypsum – rectangular, and processed phosphogypsum crystals are also of rectangular shape, but smaller comparing to that of phosphogypsum. Size of the last crystals was also influenced by phosphogypsum treatment, using the rotating magnetic field. These results are in accordance with the results of Mischenko et al [7].

The performed granulometric analysis (Fig. 3) of raw materials confirms that phosphogypsum particles are almost two-fold larger comparing to that of the processed phosphogypsum. Phosphogypsum contains 50% of particles with a diameter smaller than 70 μm. The processed phosphogypsum contains 50% of particles with the diameter smaller than 38 μm. The prevailing size of processed phosphogypsum particles is 56 μm and about 67% of particles are smaller than 56 μm. Meanwhile, particles of size 95 μm are prevailing in unprocessed phosphogypsum. This phosphogypsum contains only 46% of particles smaller than 56 μm. Particles of reagent gypsum are much smaller comparing to the processed and unprocessed phosphogypsum. Particles of 5 μm are prevailing. There are 52% of such particles.

3.2. SEM analysis of hemihydrate gypsum, hemihydrate phosphogypsum and processed hemihydrate phosphogypsum

In order to determine influence of gypsum dehydration method on the morphology of the crystals of the hemihydrate gypsum binding

material, gypsum materials were dehydrated by various methods and using microwaves.

After heating in temperature 400 °C the materials obtained by various dehydration methods, it was determined that their hydrate water contents varies in the range from 6.05% to 6.18%. Theoretically, the amount of hydrate water in hemihydrate gypsum is 6.21% [15]. Therefore, it may be stated that the obtained materials are hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum. The X-ray diffraction analysis confirms that products was obtained using different gypsum raw materials and various dehydration methods is hemihydrate gypsum. X-ray diffraction pattern of hemihydrate gypsum is given in Figure 4.
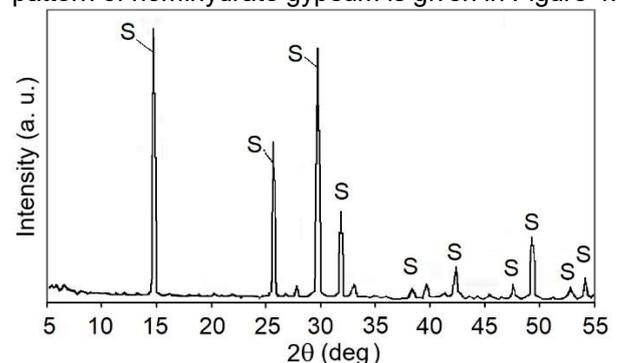

Fig. 4 – X-ray diffraction patterns of hemihydrate gypsum obtained from reagent gypsum. *Indexes:*
S – hemihydrate gypsum

When gypsum is dehydrated in the air environment, water from crystalline structure is removed as vapour. Escaping vapour disperses crystals and crystals of the resulted product become
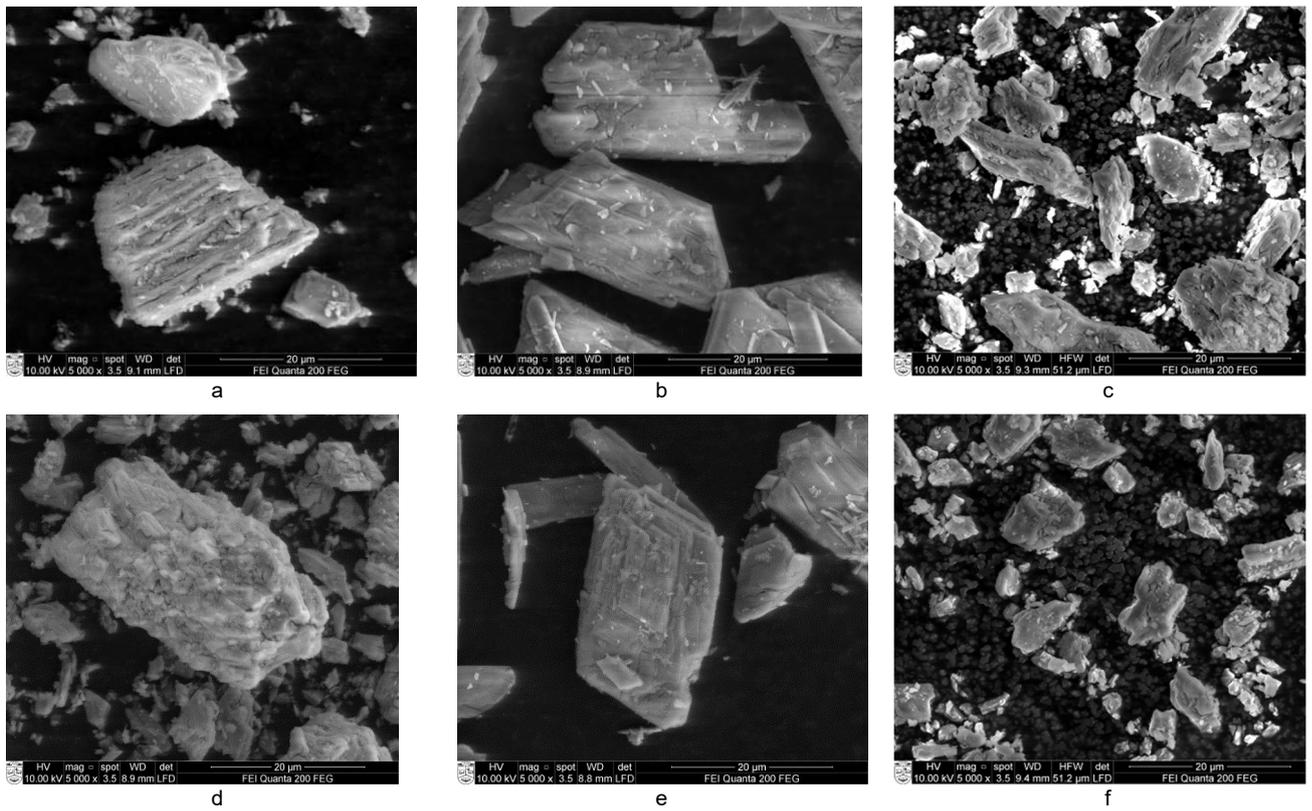
Fig. 5 - SEM analysis of hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum obtained in the convection drier (a-c) and microwave oven (d-f). a, d – from reagent gypsum; b, e – from phosphogypsum, c, f – from processed phosphogypsum.
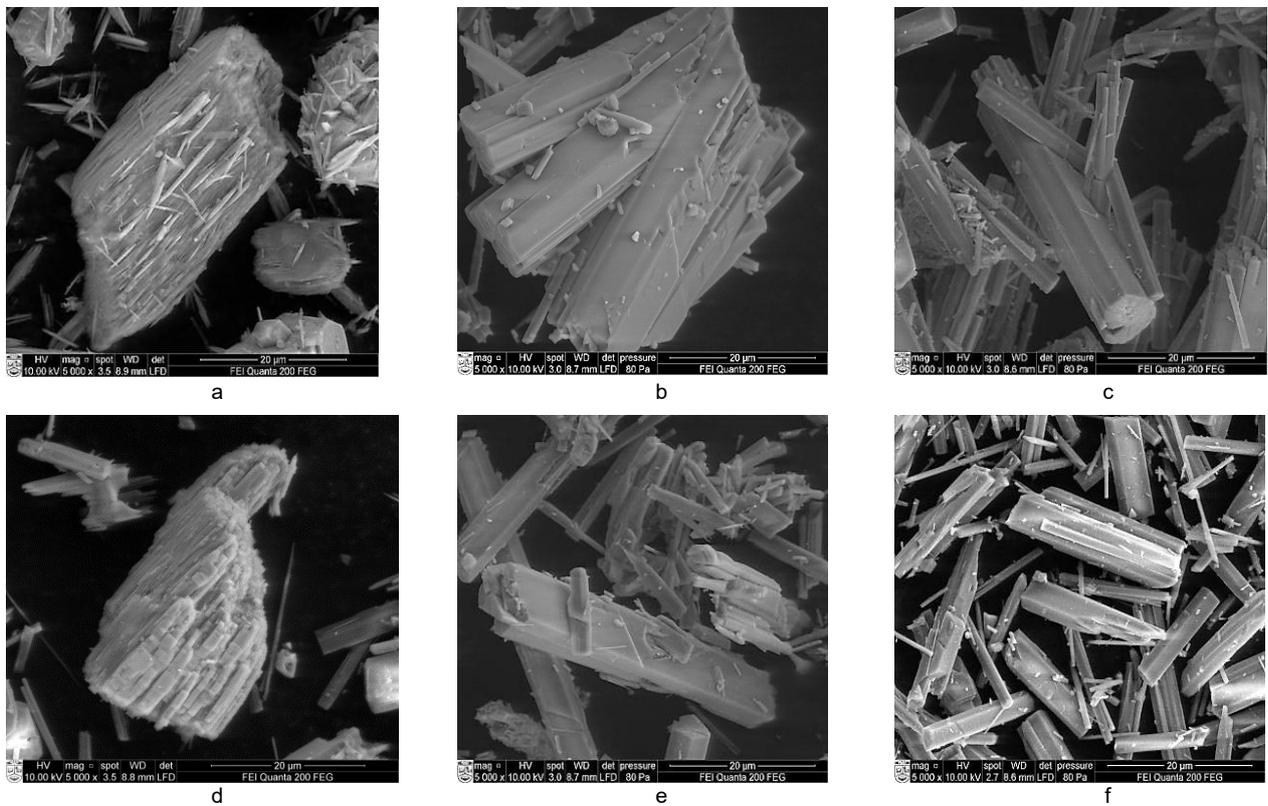

Fig. 6 - SEM analysis of hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum obtained in the autoclave (a-c) and microwave reactor (d-f). a, d – from reagent gypsum; b, e – from phosphogypsum, c, f – from processed phosphogypsum.

smaller [16]. This is confirmed by SEM analysis (Fig. 5). The hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum crystals, obtained by dehydration of various gypsum raw materials either in the convection drier or microwave oven, maintain the shape of raw material crystals. However, they are smaller comparing to that of raw material.

No significant difference was noticed between crystals obtained by using or not using microwaves for gypsum raw material dehydration. When gypsum is dehydrated in the saturated water vapour environment, gypsum dissociation and hemihydrate gypsum crystallization from solution are taking place. In such conditions, non-loose, large hemihydrate gypsum crystals are formed, which can be of needle, prism, or hexagon prism shapes [17]. Thus, the structure of hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum crystals, obtained by dehydration in the saturated water vapour environment, has to differ from hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum crystals, obtained in the air environment.

When reagent gypsum is dehydrated in the autoclave or microwave reactor, needle-shaped hemihydrate gypsum crystals grown together into agglomerates are produced (Fig. 6, a and d). When phosphogypsum is dehydrated in the autoclave or microwave reactor, prism-shaped hemihydrate phosphogypsum crystals are produced (Fig. 6, b and e). Meanwhile, when the processed phosphogypsum is dehydrated in the autoclave or microwave reactor, the produced hemihydrate phosphogypsum crystals are in the shape of regular hexagon prism (Fig. 6, c and f). It was noticed that larger crystals are produced in the autoclave independently of the raw material from which the hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum were obtained.

The results confirm that the morphology of the obtained products depends on the dehydration method of gypsum raw material. Gypsum raw material dehydration in the air environment using microwaves does not significantly influence the morphology of hemihydrate gypsum, hemihydrate phosphogypsum or processed hemihydrate phosphogypsum crystals. Meanwhile, when raw material is dehydrated in the water vapour environment using microwaves, the produced product crystals are smaller comparing to the crystals of the products obtained without using microwaves. Therefore, it may be maintained that using microwaves for gypsum raw material dehydration has no positive effect on crystals morphology.

3.3. Granulometric composition of the products obtained from different raw materials in the autoclave

The best crystallization of hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum crystals was obtained in the autoclave. The granulometric composition of the materials obtained in the autoclave was determined (Fig. 7). The results show that the particles of hemihydrate phosphogypsum obtained from phosphogypsum are the largest. Particles of diameter 21.5 μm are prevailing. Amount of such particles is almost 56.6%. Particles of hemihydrate phosphogypsum obtained from the processed phosphogypsum are almost two-fold smaller. Particles of diameter 7.5 μm are prevailing. The amount of such particles is almost 44%. Particles of 6.5 μm are prevailing in hemihydrate gypsum and the amount of such particles is almost 59%.
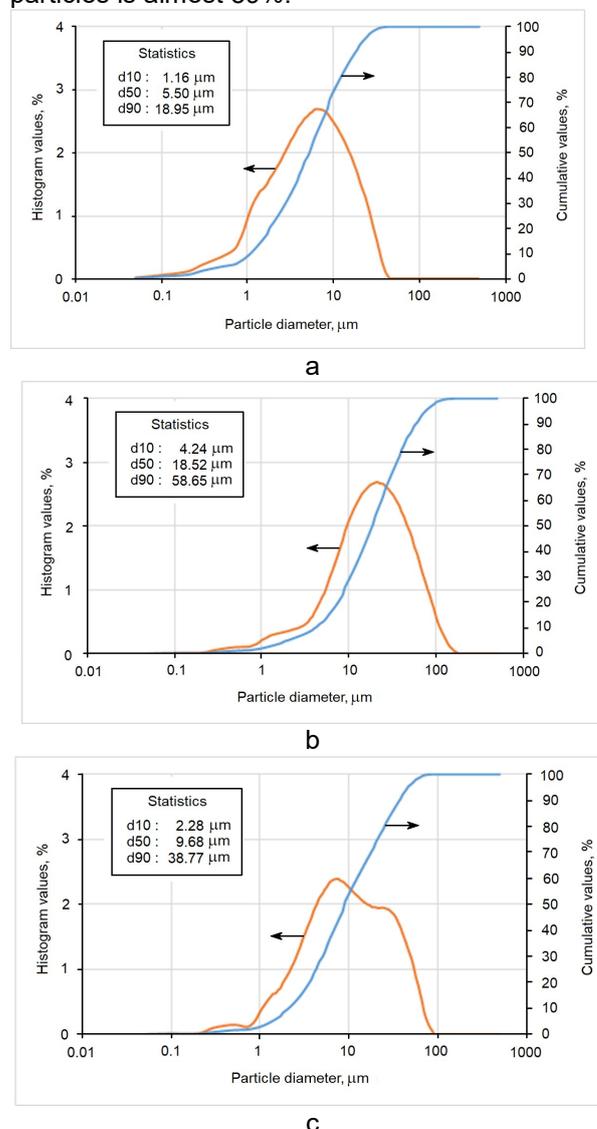

a

b

c

Fig. 7 - Particle size distribution of hemihydrate gypsum (a), hemihydrate phosphogypsum (b), and processed hemihydrate phosphogypsum (c) obtained in the autoclave.

3.4. Hydration heat

Calorimetric analysis was carried out in order to determine the hydration process of the hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum, obtained in the autoclave and microwave reactor. The heat evolution rate and total hydration heat of hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum are shown in Figure 8 and Figure 9. Heat evolution was measured for 24 hours.

Figure 8 shows only the first three hydration hours, Figure 9 shows the first nine hydration hours. No new peaks were identified further.

a

b

c

Fig. 8 - Calorimetric curves of hemihydrate gypsum (a), hemihydrate phosphogypsum (b), and processed hemihydrate phosphogypsum (c) obtained in the autoclave.

a

b

c
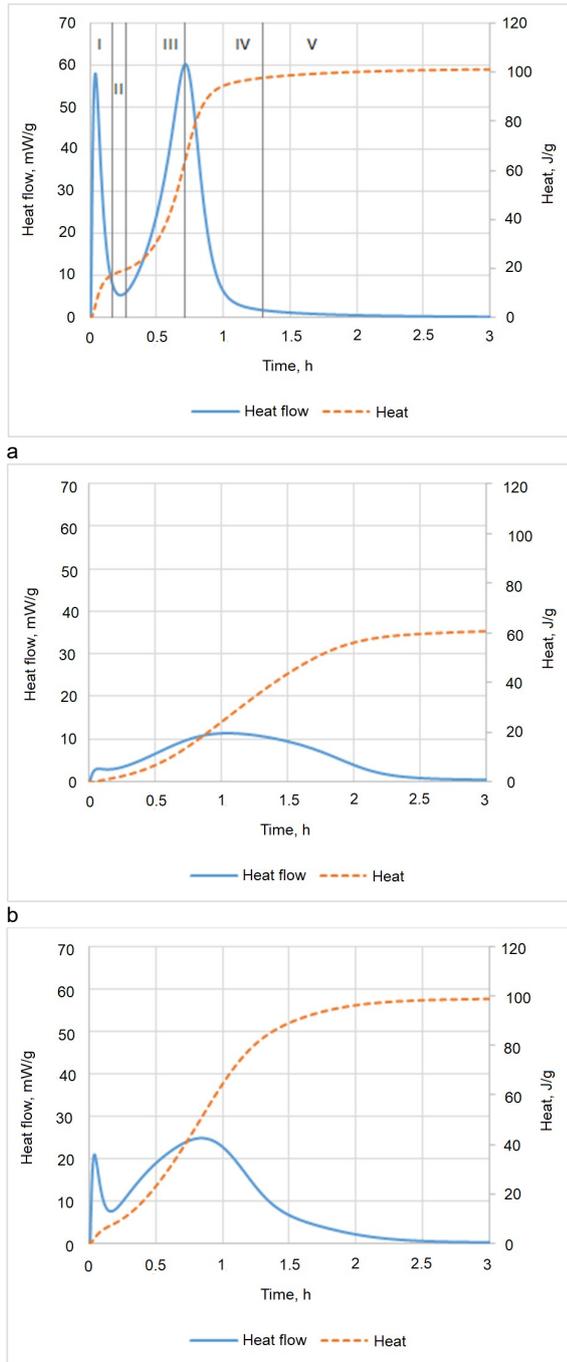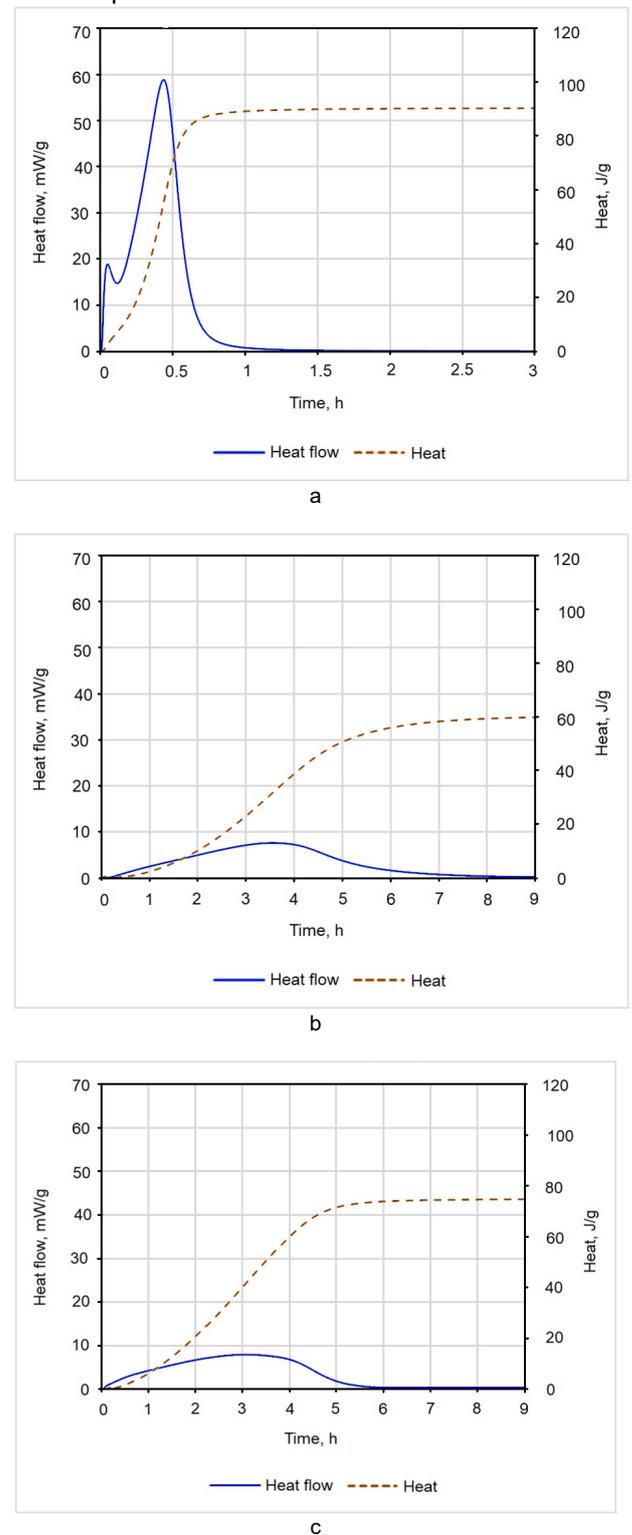
Fig. 9 - Calorimetric curves of hemihydrate gypsum (a), hemihydrate phosphogypsum (b), and processed hemihydrate phosphogypsum (c) obtained in the microwave reactor.

According to isothermal conduction calorimetry tests, hemihydrate gypsum hydration process is clearly divided into the five periods (Fig 8, a). At the beginning (period I), the initial rapid heat evolution (58 mW/g) is due to the initial wetting of the powder and dissociation of hemihydrate gypsum in Ca^{+2} and $(SO_4)^{-2}$. This was followed by the induction period (II). The rate of heat evolution reduces, the reaction slows down, dissociation of hemihydrate gypsum occurs, and formation of dihydrate gypsum starts. During period III, the reactions are accelerated and the maximum rate of heat evolution (60 mW/g) is reached after ~0.7 h. Most of the hemihydrate gypsum at this moment is converted to gypsum. During this stage, the setting is achieved. During period IV, the rate of heat flow is reduced indicating that the reactions decelerate till 1.75 h, hydration, formation, and growth of gypsum crystals are continued. Finally, gypsum hydration reaches the steady state (period V). The amount of the released heat is very low.

Data of isothermal conduction calorimetry of the processed hemihydrate phosphogypsum hydration (Fig.8, c) shows that this process is similar to hydration of hemihydrate gypsum, except that it is about three times less intensive. The rates of heat evolution represented by the first peak and the second peak are respectively 21 and 25 mW/g. The maximum rate of heat evolution of the processed hemihydrate phosphogypsum is reached after ~0.9 h.

The shape of hemihydrate phosphogypsum curves differs as above-mentioned (Fig. 8, b). During period I, the heat flow, representing the wetting of the solids and dissociation of hemihydrate phosphogypsum, has decreased to 3.1 mW/g. The maximum heat evolution rate (period III) is achieved only 11.5 mW/g after 1 hour, followed by its gradual decrease till 2.5 h of hydration. The hydration of hemihydrate phosphogypsum is significantly delayed by phosphate impurities.

The total hydration heat of hemihydrate phosphogypsum after 3 hours reaches 60 J/g. While the total hydration heat of hemihydrate gypsum and the processed hemihydrate phosphogypsum with reduced amount of impurities is, respectively 102 J/g and 99 J/g.

Data of isothermal conduction calorimetry of the hemihydrate gypsum obtained in the microwave reactor hydration (Fig.9, a) shows that this process is similar to hydration of hemihydrate gypsum obtained in the autoclave (Fig.8, a). However, the rates of heat evolution represented by the first peak and the second peak are respectively 20 and 48 mW/g. The maximum rate of heat evolution of the hemihydrate gypsum is reached after ~0.9 h.

The shape of hemihydrate phosphogypsum and processed hemihydrate phosphogypsum curves differs as above-mentioned (Fig. 9, b and c). The maximum heat evolution rate (period III) of hemihydrate phosphogypsum is achieved only 8

mW/g after 3.5 hour, followed by its gradual decrease till 8 h of hydration. Meanwhile the maximum heat evolution rate (period III) of processed hemihydrate phosphogypsum is achieved only 9 mW/g after 3 hour, followed by its gradual decrease till 6 h of hydration.

The total hydration heat of hemihydrate gypsum after 3 hours reaches 87 J/g. While the total hydration heat of hemihydrate phosphogypsum and the processed hemihydrate phosphogypsum after 9 hours is, respectively 60 J/g and 75 J/g.

Data of isothermal conduction calorimetry shows that hydration of products obtained in the autoclave occurs rather than hydration of products obtained in the microwave reactor. The obtained data allows stating that the amount of phosphate impurities has bigger influence on the hydration of hemihydrate phosphogypsum and the processed hemihydrate phosphogypsum than raw material dehydration method and morphology of product crystal.

4. Conclusions

It was identified that hemihydrate gypsum, hemihydrate phosphogypsum, and processed hemihydrate phosphogypsum are obtained when gypsum raw material is dehydrated using microwaves. However, gypsum raw material dehydration in the air environment using microwaves does not significantly influence the morphology of hemihydrate gypsum, hemihydrate phosphogypsum or processed hemihydrate phosphogypsum crystals. Meanwhile, when raw material is dehydrated in the water vapour environment using microwaves, the produced product crystals are smaller comparing to crystals of products dehydrated without microwaves. It may be stated that using microwaves for gypsum raw material dehydration has no positive effect on the morphology of the obtained product crystals. Data of isothermal conduction calorimetry shows that hydration of products obtained in the autoclave occurs rather than hydration of products obtained in the microwave reactor.

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