ISSN 1392–1320 MATERIALS SCIENCE (MEDŽIAGOTYRA). Vol. 19, No. 2. 2013

α-Hemihydrate Gypsum from Flue Gas Desulphurization Gypsum

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crossref http://dx.doi.org/10.5755/j01.ms.19.2.4438

Received 21 November 2011; accepted 15 February 2012

In this work, properties of sulphate technogenic raw material – flue gas desulphurization (FGD) gypsum have been investigated in order to obtain α-hemihydrate gypsum as gypsum binding material. FGD gypsum is produced as a by-product during the process of desulphurization of exhaust gas emitted in power stations heated by fuel containing sulphur. It has been determined that α-hemihydrate gypsum can be obtained from FGD gypsum under hydrothermal conditions at 125 °C and 130 °C. The compressive strength of gypsum samples is 13 MPa – 16 MPa after 2 h of hardening and it depends on temperature and time of isothermic curing. The compressive strength of the same samples in dry state is 49 MPa – 67 MPa. SEM analysis data showed that the properties of α-hemihydrate gypsum significantly depend on the shape and size of its crystals: when crystals have near form to regular hexagonal – shaped prism with length and width ratio approx. of 4 : 1, the gypsum exhibits the high quality mechanical and physical properties.

Keywords: flue gas desulphurization (FGD) gypsum α-hemihydrate gypsum, calcium sulphate dihydrate, dehydration, hydration.

INTRODUCTION

Portland cement is the most popular and most commonly used construction material. However, cement industry is one of the most energy-intensive industries. Extensive energy consumption is driving consumers to look for cheaper binding materials. Gypsum binder and various products based on it could be one of them. Compared to cement, gypsum production requires a considerably lower amount of fuel. Gypsum is not only produced from the natural resources which are gradually diminishing but also from alternative materials containing calcium sulphate. Flue gas desulphurization gypsum (hereinafter referred to as FGD gypsum) is one of such materials. It can be obtained as a by-product in the power plants fuelled by sulphur – containing fuel [1 – 9]. FGD gypsum is successfully processed into gypsum binders in a number of countries. The reaction of SO_2 with $CaCO_3$ or CaO in contemporary desulphurization plants produces high-quality commercial gypsum [1 – 9].

Nearly 80 % of flue gas desulphurization plants in the world apply the wet "$CaCO_3$–gypsum" method [2 – 7], involving the following reaction:

$$CaCO_3 + SO_2 + 0.5H_2O \rightarrow CaSO_3 \cdot 0.5H_2O + CO_2; \quad (1)$$

$$CaSO_3 \cdot 0.5H_2O + 0.5O_2 + 1.5H_2O \rightarrow CaSO_4 \cdot 2H_2O. \quad (2)$$

The resulting product, which does not differ from natural gypsum by its composition, has $CaSO_4 \cdot 2H_2O$ > 95 %, pH 5 – 9, whiteness > 80 %; it is odorless and non-toxic [2].

In accordance with the Lithuanian and EU normative legislation, the prohibition to burn fuel which contains more than 1 % of sulphur came into force as of 1 May 2004, or the companies are forced to install exhaust – gas desulphurization facilities [2].

Lithuanian power plant based in Elektrėnai has been equipped with modern gas desulphurization facilities producing up to 18000 tones of FGD gypsum per year for as long as several years [3]. Only after thorough tests the question whether the FGD gypsum forming in this power plant could be used for the production of gypsum binder could be answered.

The aim of the research is to determine an influence of technological parameters such as temperature and duration of isothermal curing to the crystals morphology and to the properties of α-hemihydrate gypsum.

MATERIALS AND METHODS

Flue gas desulphurization gypsum means the product obtained at Lithuanian power plant upon the desulphurization of exhaust gas by means of the wet (limestone – $CaCO_3$ slurry) method.

α-hemihydrate gypsum was obtained from FGD gypsum in rotating autoclave "Lampart" at predetermined temperature. Crystallization regulator was used pure maleic anhydride $C_4H_2O_3$. The duration of isothermal curing was varied from 15 min to 3 hours. A dehydration of gypsum has been carried out in water/gypsum suspension. After the process of synthesis a product was filtrated and dried.

To evaluate mechanical properties (compressive strength) of α-hemihydrate gypsum, from normal slurry consistence gypsum we have formed 2×2 cm cubes, which were compressed by press ELE AutoTest. The setting time was determined by using Vicat apparatus.

The hydration water content in gypsum (HW), % was calculated after heating the material at the temperature 400 °C. The hydration of the gypsum binder was impeded at some selected time intervals (after 2 hours; after 1 day) by grinding the substance in the porcelain mortar, adding acetone, by filtration and drying at 50 °C.

The X-ray diffraction analysis of the substances was performed using the X-ray diffractometer DRON-6. CuK_α

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radiation and Ni filter were used. The powder X-ray diffraction patterns of materials were identified with references available in PDF-2 data base [10].

Simultaneous thermal analysis (STA: differential scanning calorimetry – DSC and thermogravimetry – TG) was carried out on a Netzsch instrument STA 409 PC using a heating rate of 15 °C/min. The temperature ranged from 30 °C up to 1000 °C under an air atmosphere. The ceramic sample handlers and crucibles of Pt-Rh were used.

The scanning electron microscopy (SEM) of the materials was performed using FEI QUANTA 200 FEG microscope.

The specific surface area (S_a) of the substances was determined by the Blaine's method.

The pH measurements of water suspensions were conducted by pH-meter 673 M, when the ratio of water (W) and solid material (S) W/S – 10.

The chemical composition was determined using classical methods of the chemical analysis.

RESULTS AND DISCUSSION

α-hemihydrate gypsum can be obtained from dihydrate calcium sulphate ($CaSO_4 \cdot 2H_2O$) in two ways: 1) in acid or saline solutions [9 – 16]; 2) in the saturated water vapour conditions [17 – 19]. The data given in literature show that the properties of gypsum binder, obtained from technogenic raw material, and the morphology of hemihydrate calcium sulphate crystals do not only depend on the type of raw material and purity but also on the technological parameters: temperature, duration of isothermal curing and additives used. Therefore, the tests revealed that these factors influence the crystal structure of α-hemihydrate gypsum obtained from FGD gypsum and its physical-mechanical properties [8, 13, 14, 16, 20, 21].

The data of the chemical analysis of FGD gypsum raw material provided in Table 1 show that this type of gypsum is almost a pure dihydrate calcium sulphate [2] (approx. 99.2 % $CaSO_4 \cdot 2H_2O$) with pH indicator close to neutral (6.9).

Table 1. The mean chemical composition of FGD gypsum (wt.%)

Material	CaO	SO_3	R_2O_3	SiO_2	Loss of ign.
FGD gypsum	32.42	46.04	0.12	0.65	20.77

The data obtained by means of various methods of instrumental analysis also confirm the following findings.

As the X-ray diffraction pattern (Fig. 1) and STA curve (Fig. 2) of the FGD gypsum show, these materials are dominated by dihydrate calcium sulphate $CaSO_4 \cdot 2H_2O$.

Microphotographs (Fig. 3) show, that dihydrate gypsum $CaSO_4 \cdot 2H_2O$ crystals of FGD are rod-shaped crystals (Fig. 3, a, and Fig. 3, b) [20].

In considering a lower energy costs, FGD gypsum dehydration has been carried out under hydrothermal conditions at 110 °C – 130 °C temperature when the duration of isothermal curing was up to 3 h.

It is essential to use crystallization regulators in order to obtain the gypsum binder (α-hemihydrate gypsum) characterized by good physical-mechanical properties in the process of dehydration of dihydrate gypsum under hydrothermal conditions.

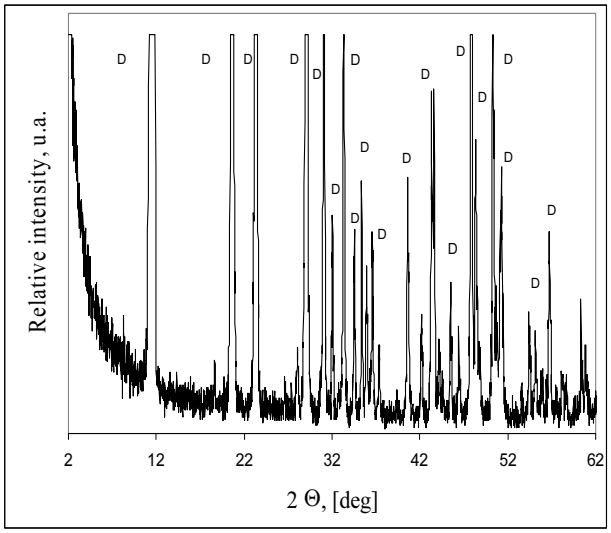


Fig. 1. X-ray diffraction pattern of the raw materials (FGD gypsum). Indexes: D – $CaSO_4 \cdot 2H_2O$

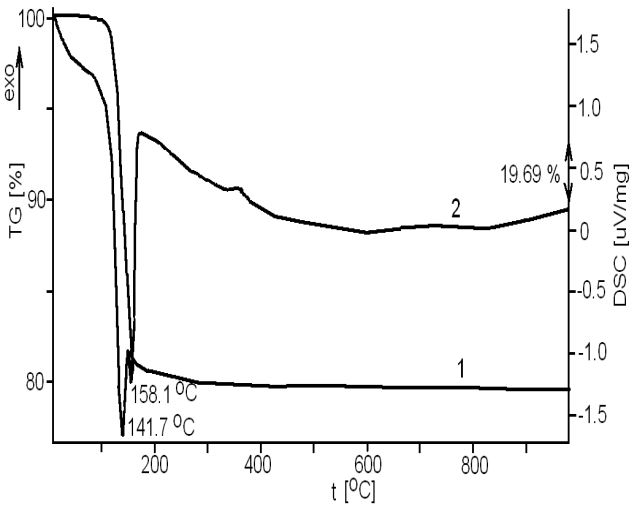
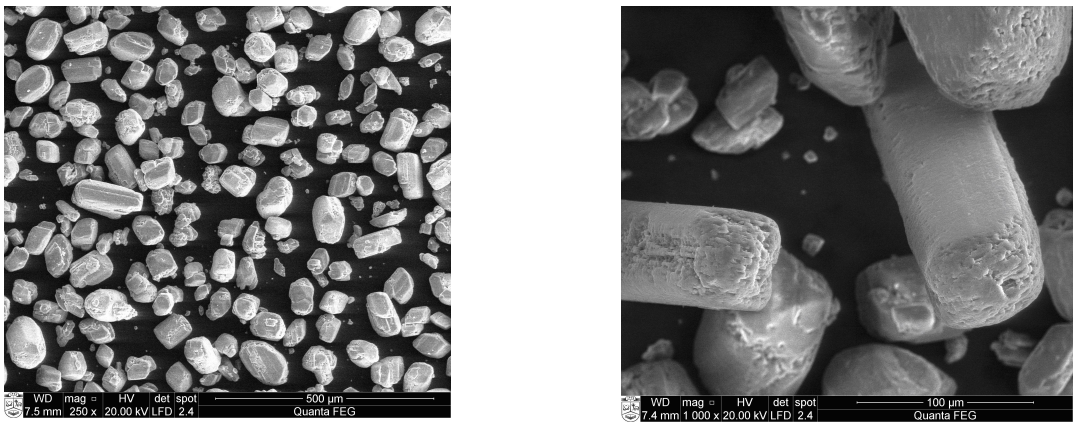


Fig. 2. STA curve of the raw materials (FGD gypsum). TG – 1, DSC – 2

The previous tests showed that the additive of maleic anhydride (0.1 %) is best for crystallization of α-hemihydrate gypsum from dihydrate [19].

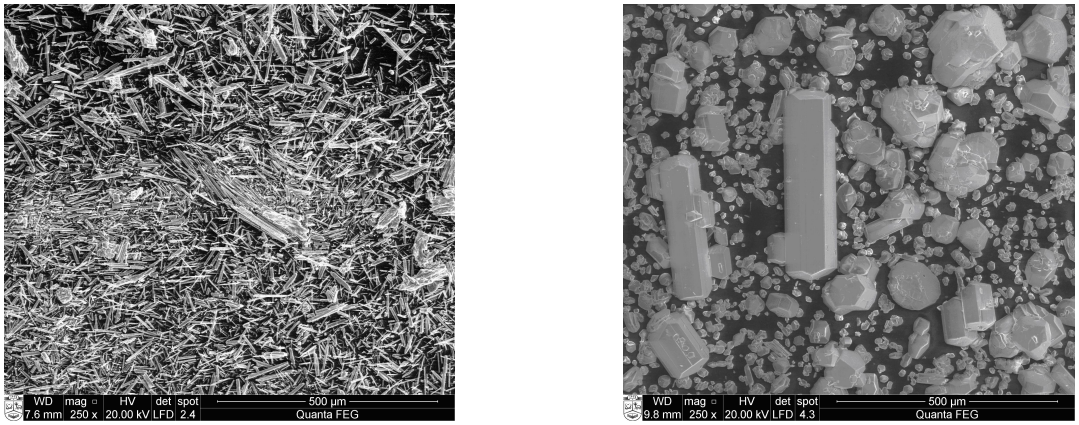
Fig. 4, a, shows that the α-hemihydrate gypsum obtained without crystallization regulator is composed of densely-arranged intertwined long-needle-shaped crystals. The addition of maleic acid anhydride crystallization regulator stops the crystal growth in one direction; therefore, crystals can grow until they acquire a shape of large prism crystals (Fig. 4, b). [21]

We have already drawn conclusions on the process of dehydration of dihydrate gypsum by determining the hydration water (HW) in samples, which was gradually decreasing. In theory [22], the hydration water (HW) in dihydrate gypsum $CaSO_4 \cdot 2H_2O$ amounts to 20.93 %, whereas in hemihydrate $CaSO_4 \cdot 0.5H_2O$, its amount must reduce to 6.2 %.



a b

Fig. 3. SEM microphotograph of the crystals of FGD gypsum ($CaSO_4 \cdot 2H_2O$); a, b – different magnification



a b

Fig. 4. SEM microphotograph of α-hemihydrate gypsum produced as follows: a – without a crystallization regulator; b – with the 0.1 % amount of maleic acid anhydride

The kinetic curves of dehydration of the samples under analysis are given in Fig. 5.

As illustrated by the X-ray diffraction patterns in Fig. 6, the higher dehydration temperature, the shorter isothermal curing is required for the dihydrate to turn to hemihydrate in full.

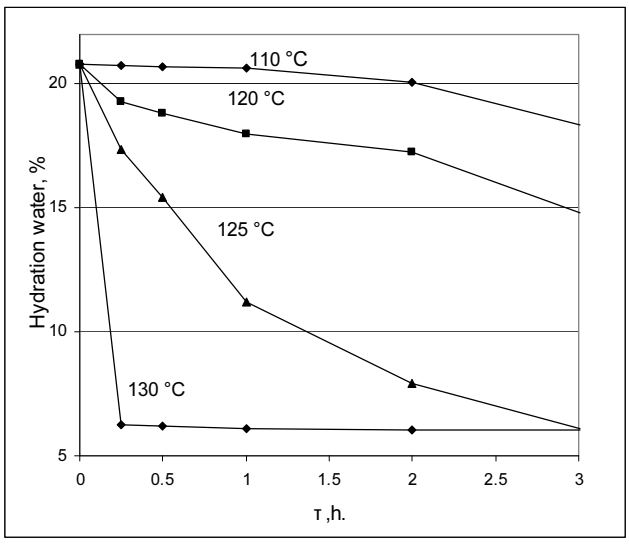


Fig. 5. Dehydration (HW) kinetics of the FGD gypsum at different temperatures

We may assert that when the temperature is low (up to 120 °C), the dehydration process is particularly slow and cost-inefficient. When the temperature is increased to 125 °C, dehydration accelerates, resulting in hemihydrate gypsum after only 3 hours of curing. The X-ray diffraction patterns (Fig. 6) confirm the data obtained. The data of tests show that when the temperature is set to 130 °C, it takes only 30 min for α-hemihydrate gypsum to form, whereas longer processing allows us to obtain more uniform and larger crystals, i. e. the specific surface area reduces (Table 2).

When analyzing the X-ray diffraction patterns of the materials obtained at 125 °C, we notice the presence of both hemihydrate ($CaSO_4 \cdot 0.5H_2O$) and dihydrate ($CaSO_4 \cdot 2H_2O$) calcium sulphate in dehydrated sample (HW = 11.21 %) after the isothermal curing for 1 hour. After curing for 2 hours the mixture of $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 0.5H_2O$ also are observed (HW = 7.92 %), though the "diffraction peaks" of dihydrate calcium sulphate are on a downward trend and they are no longer that intensive. The X-ray diffraction pattern of the samples processed at the temperature of 125 °C for 3 hours shows only hemihydrate-characteristic diffraction patterns maximums, which confirms that the result is pure α-$CaSO_4 \cdot 0.5H_2O$ (HW = 6.2 %).

When the temperature of isothermal curing of samples is increased to 130 °C, the pure $CaSO_4 \cdot 0.5H_2O$

(HW = 6.2 %) is obtained from FGD gypsum after 30 minutes of curing.

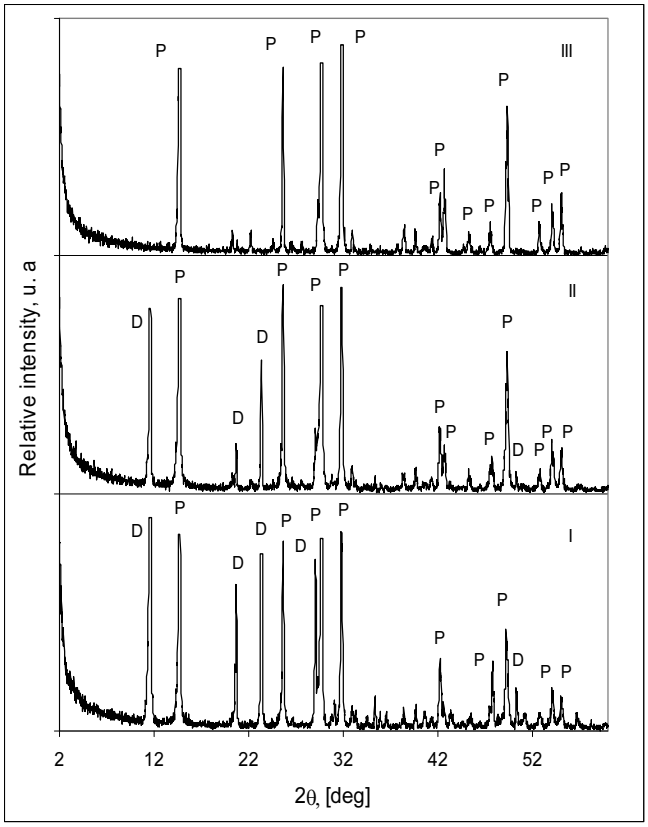


Fig. 6. X-ray diffraction patterns of the gypsum obtained at the temperature 125 °C, when isothermal duration time: I – 1 h; II – 2 h; III – 3 h. Indexes: P – $CaSO_4 \cdot 0{,}5H_2O$; D – $CaSO_4 \cdot 2H_2O$

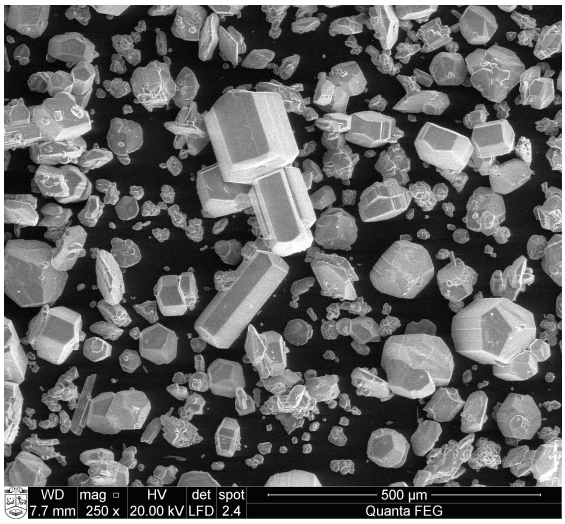
The microscopic analysis of the material obtained was carried out in order to evaluate the parameters of the paramount importance to the physical-mechanical properties of gypsum binder. The specific surface area was identified and other standard gypsum binder tests were carried out.

The results of SEM tests given in Figs. 7 – 9 show that the temperature of hydrothermal processing and the duration of isothermal curing of gypsum determine the crystal structure of the material formed, which affects the physical-mechanical properties of samples (Table 2.)

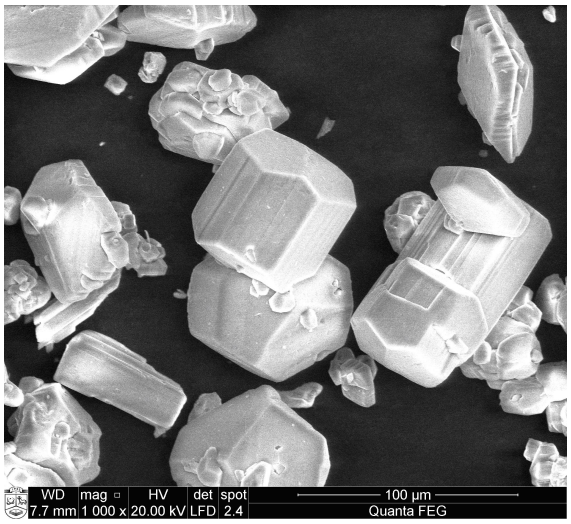
SEM microphotographs of hemihydrate formed at the temperature of 125 °C after 3 hours of curing given in Fig. 7 show that the crystal material of dense structure and prism shape [13, 14] was obtained. The compressive strength of the samples formed from this material after 2 hours of hardening was 15 MPa and 49 MPa for dry samples.

The analysis of test results of the material obtained at higher temperature of 130 °C shows that isolated large short hexagonal prism-shaped crystals [13, 14] form after 0.5 hours of dehydration (Fig. 8) with a number of various, sometimes irregular-shaped, small crystals among them. The compressive strength of the samples formed from this material after 2 hours of hardening were 13 MPa and 49 MPa for dry samples When the duration of isothermal curing is extended, smaller crystals dissolve and recrystallize, thus forming larger hemihydrate crystals; their specific surface area and W/G reduce. Therefore, the compressive strength of samples increases. The best strength properties were exposed by the samples formed from the material obtained at 130 °C after 3 hours of isothermal curing. The crystals of this material were the largest (Fig. 9); they had a shape of a regular hexagonal prism [21] (length and width ratio approx. of 4 : 1, specific surface area $S_a = 27$ m^2/kg), least water amount was required to mix it (W/G = 0.27) and it showed the largest density in samples.

The data of SEM analysis lead to a conclusion that the level of material decrystallization depends on the duration of its hydrothermal processing. Longer duration of isothermal curing at high temperature results in regular, large α-hemihydrate gypsum hexagonal prisms, therefore, the specific surface area of the material and W/G reduces and compressive strength increases. The gypsum binder of such properties should find a broad application in construction [8, 21, 23].

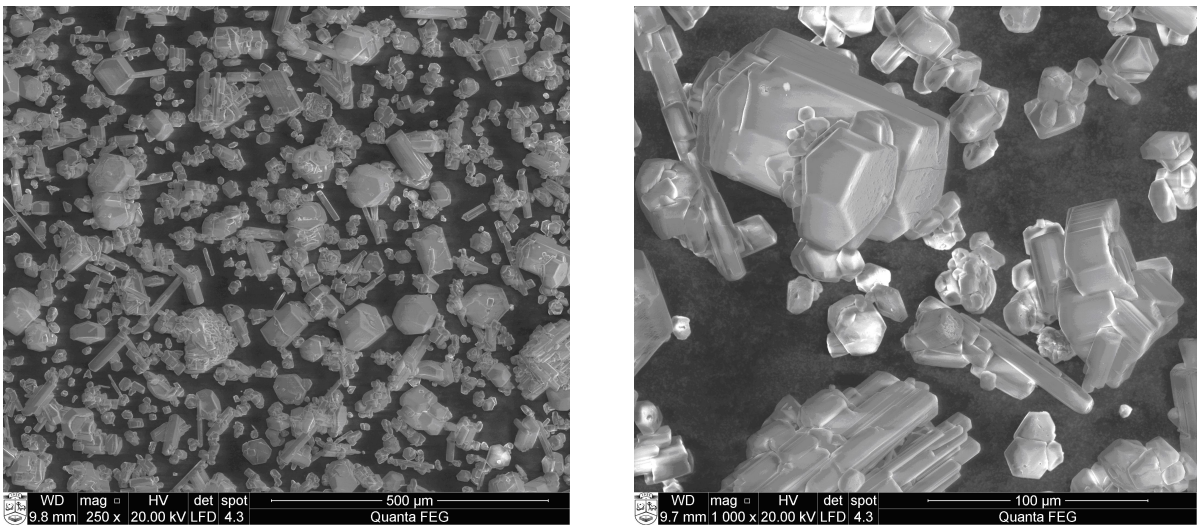


a



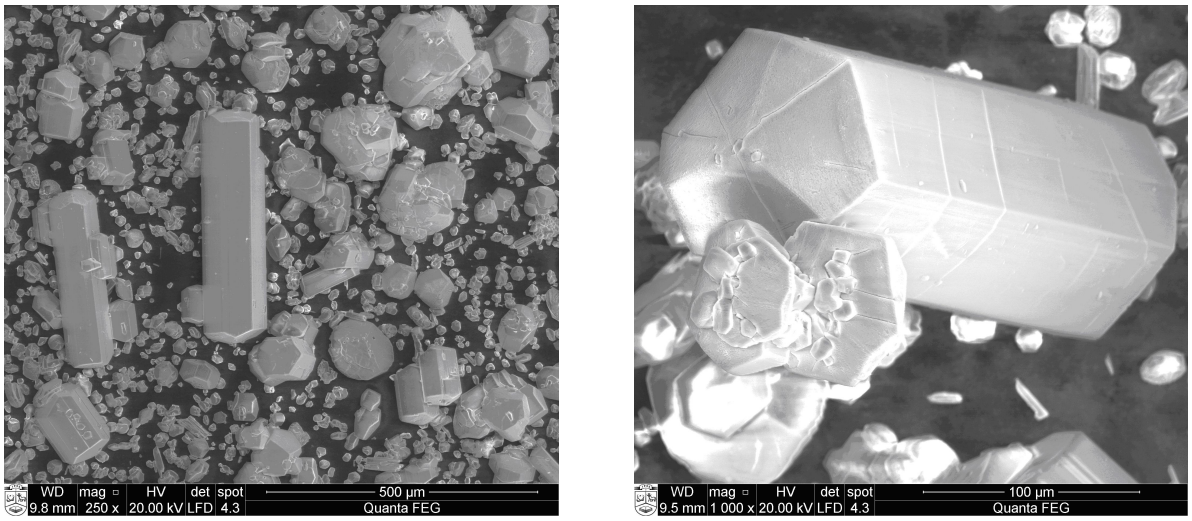
b

Fig. 7. SEM microphotographs of the crystals of α-$CaSO_4 \cdot 0.5H_2O$ obtained at 125 °C after 3 hours of dehydration of FGD gypsum; $S_a = 29$ m^2/kg; a, b – different magnification



a b

Fig. 8. SEM microphotographs of the crystals of α-$CaSO_4 \cdot 0.5H_2O$ obtained at 130 °C after 0.5 hours of dehydration of FGD gypsum; S_a = 33 m^2/kg; a, b – different magnification



a b

Fig. 9. SEM microphotographs of the crystals of α-$CaSO_4 \cdot 0.5H_2O$ obtained at 130 °C after 3 hours of dehydration of FGD gypsum; S_a = 27 m^2/kg; a, b – different magnification

Table 2. Physical-mechanical properties of the samples formed from hydrothermally processed FGD gypsum

Duration of isothermal curing, h	S_a m^2/kg	W/G	Setting time, min		Compressive strength, MPa		
			Initial.	Final	2 hour	1 day	Dry samples
Dehydration at 125 °C temperature							
3	29	0.33	12	16	15	27	49
Dehydration at 130 °C temperature							
0.25	34	0.31	21	24	11	24	48
0.50	33	0.31	15	18	13	25	49
1	33	0.30	15	18	16	26	50
2	31	0.29	15	18	16	27	60
3	27	0.27	14	17	16	28	67

CONCLUSIONS

1. After extensive investigation of FGD gypsum, it was determined that it has more than 99 % of $CaSO_4 \cdot 2H_2O$. The morphology of gypsum shows predominantly rod shaped crystals, which size is 100 μm – 150 μm.
2. The gypsum binder, which exhibits high quality physical and mechanical properties, based on α-hemihydrate gypsum can be obtained from the FGD gypsum under hydrothermal conditions. The isothermal temperature and duration of curing has significant influence to the properties of binder. The best properties of binder was find in gypsum, obtained in hydrothermal conditions at 130 °C during 3 hours of isothermal curing. The compressive strength of dry samples reached to 67 MPa. Sufficiently good properties were exposed by α-hemihydrate gypsum obtained in hydrothermal conditions at 125 °C after 3 hours of isothermal curing, or after 30 min of curing at 130°C. The compressive strength of the samples formed from these gypsum binders after 2 hours of hardening reached 13 MPa – 15 MPa, meanwhile the compressive strength of dry samples was 49 MPa.
3. Analysis of SEM data of gypsum binder showed that the properties of α-$CaSO_4 \cdot 0.5\ H_2O$ are determined by the shape and size of its crystals. The largest regular hexagonal-shaped prisms hemihydrate crystals (length and width ratio of 4 : 1) were obtained after 3-hour hydrothermal curing of FGD gypsum at 130 °C.

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