Structurally controlled synthesis of calcium sulphate dihydrate from industrial wastes of spent sulphuric acid and limestone

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ABSTRACT

All types of gypsum binders are obtained mainly from the natural gypsum and man-made products. As a sustainable analogue of these materials, synthetic gypsum as a product of spent dilute sulphuric acid and calcium carbonate was proposed. We investigated the effect of various technological parameters on the production of calcium sulphate dihydrate particles with a given morphology. The sizes of calcium sulphate dihydrate crystals with optimal values of technological parameters and exposure time up to 4.5 h increased from 18 to 28 μm and combined into agglomerates with sizes that mostly lie in the range from 200 to 600 μm. Synthesized calcium sulphate crystals acquiring a prismatic shape instead of a needle shape which simplified and accelerated the industrial filtration process. Our study shows that a promising sustainable and cheap source of gypsum-containing raw materials is synthetic gypsum, obtained by reacting a suspension of calcium carbonate and spent sulphuric acid.

1. Introduction

More than 50 types of gypsum-containing wastes are known in the world, among them are phosphogypsum and sulfo-gypsum produced on a large-scale. The number of technological schemes in the world for the processing of phosphogypsum for various gypsum binders has been developed, but for economic reasons, only 2%–3% of this man-made product is processed into gypsum binders and other building materials according to the UN (Saadaoui et al., 2017). This unsatisfactory recycling situation is caused by the required multistage neutralization of impurities, including radioactive isotopes, during the preparation of phosphogypsum prior to its next processing. In addition to the fact that phosphogypsum contains acidic phosphate impurities, the phosphogypsum obtained by the "dihydrate" technology forms needle-like crystals, which negatively affects the properties of gypsum binders (Rajkovic and Toskovic, 2002).

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An economic analysis compared the cost of sulfo-gypsum as a raw material with that of natural gypsum (Anon, 2010). In Western European countries natural gypsum cost 10–15 US dollars per ton, and the cost of synthetic gypsum is 3.5–5.0. In the United States, the cost of gypsum produced by desulphurization is 8.0–9.5 US dollars/ton, and its production is constantly growing to currently about 700 thousand tons per year.

Besides the content of the main substance, also the properties of the crystal lattice (Li et al., 2017) like the morphology of $CaSO_4 \cdot 2H_2O$ crystals, and the density of the gypsum stone are important to the properties of the gypsum binder. These characteristics vary in general not only in the raw materials of various deposits but also within the area of one deposit. This is the main reason for the difficulties associated with managing the technological process of producing building and high-strength gypsum binders. Therefore, recently attempts have been made to develop scientific approaches in assessing the quality of gypsum in materials, as well as obtaining the necessary crystal shape (Massaro et al., 2010).

In the preparation of synthetic gypsum, various types of raw materials were used, beginning from different wastes and ending with synthetic materials. Thus, methods for the production of $CaSO_4 \cdot 2H_2O$ by neutralizing wastewater containing H^+ and SO_4^{2-} ions in a significant amount were described in patents (Anon, 0000a,b,c,d,e,f). However, due to the presence of a significant amount of impurities, the resulting synthetic gypsum is only recommended as filler in the production of insulating and fire-resistant materials, paper, paints, synthetic resins, etc.

Analysis of literature shows that the properties of the gypsum binder to a certain extent depend on the size and shape of the original $CaSO_4 \cdot 2H_2O$ (Li et al., 2017; Massaro et al., 2010; Alimi and Gadri, 2004). With increasing crystals of calcium sulphate dehydrate, their shape becomes closer to the cubic and moves away from the needle-shape, lead to less water consumption and the higher binder strength.

In addition, the precipitate of calcium sulphate dihydrate must have good filterability in order to ensure low costs, and this property also depends on the shape and size of the product crystals. Gypsum obtained from natural raw materials may be heterogeneous in strength, and this is due to, (i) the crystal-chemical features of the gypsum stone, (ii) the different morphology of gypsum crystals, and (iii) the presence of various impurities in their structure. The production of synthetic gypsum can be oriented towards obtaining crystals of a given morphology, and therefore, high strength properties of gypsum binder can be obtained.

In the production of gypsum, as in any other production, environmental aspects are important. Sustainable production of materials based on industrial waste is therefore advantageous. In the production of gypsum from raw materials based on waste, e.g. spent dilute sulphuric acid can be considered, which is formed at a number of chemical enterprises. For the purpose of utilization, the acid is subjected to additional dilution, then neutralized and often discharged into the environment, since the regeneration process is very expensive. Another waste can be used in the process, such as sifting out a small fraction of limestone, which is produced at sugar factories, metallurgical plants and lime plants in shaft furnaces. This limestone waste accumulates today often in dumps of large areas of useful land. In addition to the use of waste in the production of gypsum, it is necessary that this production is optimized to the most comprehensive use of raw materials to reduce the impact on the environment.

Obtained calcium sulphate dihydrate can be used in processing technologies for gypsum binders, production of composite materials for construction and technical purposes, as well as in medicine (e.g. for treatment of fractures), or in other technologies where calcium sulphate dihydrate is needed.
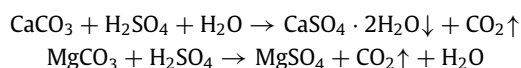
2. Materials and methods

2.1. Materials

For the production of synthetic gypsum, waste derived diluted sulphuric acid obtained from the production of heat-resistant fibres was applied together with water and chalk. The spent dilute sulphuric acid is an oily yellowish liquid with a density of 1.41–1.43 g/cm^3 at 25 °C and a concentration of 53–55 of sulphuric acid wt.% in the waste. It contains organic impurities, including terephthalic acid (up to 0.014 wt.%), hydrosinsulphate (up to 2.5 g/L) and iron in the amount of 55–58 mg/L. The chemical composition (in wt.%) of chalk is $CaCO_3 + MgCO_3$ (where $CaCO_3$ is 95.57); $CaCO_3$ − 94.5; $Fe_2O_3 + Al_2O_3$ − 0.21; others. − 1.98; H_2O − 0.48; Water: iron content − 0.3 mg/L; Permanganate oxidability − not more than 5 mg O_2/L; pH − 6.0–9.0.

2.2. Sample preparation

Calcium sulphate dihydrate was precipitated by mixing sulphuric acid and a chalk suspension in a reactor with constant stirring at a stirrer rotation speed of 90–150 rpm and constant heating to 40–60 °C. The driving force of crystallization was supersaturation in the reaction system. The completeness of the precipitation reaction was ensured by the end of the gas evolution and by the change in the pH of the reaction mixture. During decomposition of chalk with sulphuric acid, the following chemical reactions occur:

$$CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4 \cdot 2H_2O\downarrow + CO_2\uparrow$$
$$MgCO_3 + H_2SO_4 \rightarrow MgSO_4 + CO_2\uparrow + H_2O$$

Table 1
Particle size distribution of synthetic gypsum.

Particle size (μm)	The fraction content (wt.%)		
	Minimum	Maximum	Average value ± SD
0.05–1.0	0.50	0.85	0.73 ± 0.20
1.0–2.0	0.34	0.81	0.65 ± 0.27
2.0–3.0	0.66	1.01	0.79 ± 0.19
3.0–4.0	0.23	0.49	0.32 ± 0.15
4.0–5.0	0.11	0.26	0.17 ± 0.08
5.0–10.0	2.18	4.51	2.98 ± 1.33
10.0–20.0	1.71	8.91	4.75 ± 3.73
20.0–50.0	4.07	13.11	7.60 ± 4.83
50.0–100.0	1.98	5.62	3.39 ± 1.96
100.0–200.0	0.08	0.82	0.33 ± 0.42
200.0–600.0	76.33	80.08	78.31 ± 1.88

Due to the fact that the chalk contains clay minerals (kaolinites) Al_2O_3 (Fe_2O_3 $2SiO_2 \cdot 2H_2O$) – the following reactions also take place during the decomposition of chalk with sulphuric acid (SiO_2 – insoluble impurity):

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O,$$
$$Al_2O_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 3H_2O.$$
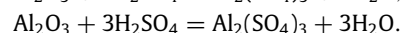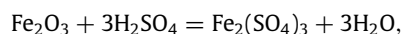
Then a solution of sulphuric acid at a concentration of 53–55 wt.% is prepared and fed into the reactor at a rate of 0.55–0.85 L/h to the chalk suspension, which is constantly stirred with a speed of 25–35 rad/min. The temperature inside the reactor is maintained in the range of 40–60 °C. The reaction ends when a neutral pH is obtained and CO_2 stops to produce. Next, suspension of calcium sulphate dihydrate is added that acts as an agglomerating agent. The suspension, with constant stirring, is aged for 2.5–4 h in order to increase the calcium sulphate dihydrate particles size. After this time, the suspension is filtered, separating calcium sulphate dihydrate from the bittern. The resulting calcium sulphate dihydrate cake is dried, and the bittern is passing on to the preparation stage with the chalk suspension.

2.3. Surface morphology and composition

Morphology and elemental composition of the sample surface were investigated by the scanning electron microscopic (SEM) analysis with Hitachi Field Emission Scanning Electron Microscope SU-70 (Japan), equipped with the X-Max Silicon Drift Detector (SDD) (Oxford Instruments, England) for using of energy-dispersive X-ray spectroscopy (EDX/EDS). At least two samples were investigated for each condition.

The phase composition of the synthesized solid phase was determined by using a X-ray diffraction analysis with Panalytical X'PERT PRO diffractometer (Netherlands) (wavelength Cu Kα (1.5405 A) and software Philips X'PERT suite). Rietveld refinements were conducted with the software HighScore Plus. The pseudo-Voigt function was used for the peak profile refinement. The average size of crystalline grains of synthesized materials was calculated by the Scherrer Eq. (1):

$$d = K \cdot \lambda / \beta \cdot \cos \theta \tag{1}$$

where $K = 1$, $\lambda = 0.155418$ nm (CuKα line), β is the width of reflection at half-height, and θ is the angle of diffraction.

Thermogravimetric analysis (TGA) was performed in a TA Q500 instrument. Approximately 20 mg of the sample was placed into an alumina pan without a lid and heated from ambient temperature to 1000 °C at 10 °C/min under a nitrogen purge flow of 100 cm^3/min.

3. Results and discussion

The shape and size of the crystals of obtained calcium sulphate dehydrate were investigated as a function of the type of water used for the preparation of the suspension. The particle size distribution is presented in Table 1:

In the synthesis of synthetic calcium sulphate dihydrate, particles of different sizes (fractions) were obtained. The target fraction of the resulting synthetic gypsum is a fraction of more than 20 μm, as is necessary to obtain a successful filtration step. From the data obtained, 89.63 ± 5.19 wt.% is filtered, while the remaining fraction of smaller particles remain in the mother liquid, and can be used as seed crystals in subsequent syntheses.

In a preliminary series of experiments, it was found that the composition of water used for the preparation of a suspension of calcium carbonate is very important (Table 2).

The corresponding water compositions used for the synthesis are presented in Table 3.

The obtained data of chemical analysis of the different types of waste show that the metal ions/species contained in the water used for the preparation of calcium carbonate suspensions in different quantities influence the formation of crystals and particles of synthetic calcium sulphate dihydrate. It was found that calcium sulphate dihydrate obtained using artesian water had prismatic crystals with larger sizes compared to the other two types of water. Proceeding from

Table 2
Variance of synthetic gypsum obtained from different types of water suspensions.

Particle size (μm)	Fraction content (wt.%)				
	River	Distilled	Artesian	min	max
0.05–1.0	0.0	0.17	1.39	0.0	1.39
1.0–2.0	2.67	0.79	1.29	0.79	2.67
2.0–3.0	7.64	0.38	0.79	0.38	7.64
3.0–4.0	4.08	0.43	1.3	0.43	4.08
4.0–5.0	2.16	0.54	1.05	0.54	2.16
5.0–10.0	1.24	1.11	4.67	1.11	4.67
10.0–20.0	0.03	7.2	2.31	0.03	7.2
20.0–50.0	55.43	7.63	0.63	0.63	55.43
50.0–100.0	26.31	9.96	0.0	0.0	26.31
100.0–200.0	0.44	2.96	7.16	0.44	7.16
200.0–600.0	0.0	68.83	79.41	0.0	79.41

Table 3
Chemical composition of water used for synthesis.

Element	Element content in water		
	River	Distilled	Artesian
Al	0.0188	–	0.0404
B	0.0117	–	0.0355
Ba	0.0497	0.0021	0.2192
Ca	50.78	1.216	77.95
Fe	0.0112	0.0067	0.0117
K	17.49	17.93	33.51
Li	0.0022	–	0.0053
Mg	11.74	0.2919	20.61
Mn	0.0123	0.0044	0.0127
Na	6.947	1.127	5.178
S	3.866	0.0121	0.5501
Si	2.248	0.4589	6.523
Sr	0.1075	0.0046	0.1416
Zn	0.0207	0.0043	–

– Below limit of detection.

this, metal species contribute to the formation of the structure in decreasing order: Al; B; Ba; Ca; Fe; K; Li; Mg; Mn; Na; S; Si; Sr; Zn.

From the EDX data obtained, it is clear that the ratio by atomic mass between Ca and S is approaching 1: 1 (wt.%: Ca − 11.40 ± 0.58; S – 11.92 ± 0.73), which proves that the resulting material from spent sulphuric acid and calcium carbonate is $CaSO_4 \cdot 2H_2O$.

The crystallization of calcium sulphate dihydrate has been subject of several studies on factors that have a significant effect on the precipitation, including temperature, supersaturation, the effect of organic and inorganic additives (Alimi and Gadri, 2004; Hamdona and Al Hadad, 2007). Despite considerable research of calcium sulphate formation in the aquatic environment, many uncertainties remain, including factors that make it possible to obtain particles of calcium sulphate dihydrate of a given shape and size, as well as to obtain intergrowths of crystals.

There is a relationship between the size and shape of the crystals and the strength characteristics of the binder. This is explained by the fact that in this mode, a larger number of big pragmatically shaped crystals of $CaSO_4 \cdot 2H_2O$ (Fig. 1) are formed compared to other synthesis conditions, under which mainly crystals with a needle-like shape of large length and small width are formed (Luo et al., 2010). Optimal parameters of the production of synthetic gypsum from spent sulphuric acid and calcium carbonate enabled to obtain crystals of a prismatic form, not a needle, as can be seen in Fig. 1. The crystals of this form are optimal for the filtration stage (centrifugation), since crystals of a needle-shaped form are lighter than prismatic crystals and therefore penetrate holes in the centrifuge grid and reduce the yield of the useful product ($CaSO_4 \cdot 2H_2O$).

The authors of Kamalipour et al. (2017), Jamialahmadi and Muller-Steinhagen (2008), Klepetsanis et al. (1990), Mahmoud et al. (2004) and Abdel-Aal et al. (2004) obtained calcium sulphate dihydrate crystals by the method of controlled synthesis, but the crystals were obtained separately. In our study, a distinctive feature was obtained — calcium sulphate dihydrate crystals were obtained as intergrowths (particles), thereby the resulting particles became larger which also optimized the stage of centrifugation and increased the strength characteristics of a binder.

Fig. 3 presents diffraction patterns of synthesized material processed by the Rietveld method. Analysis of the obtained data showed that the sample was gypsum with a monoclinic structure with space groups *C12/c1* and characteristic peaks (020), (021), (040) and (041). Peak positions and parameters of crystal cells were in a good agreement with appropriate JCPDS data (PDF 00-033-0311) and indicate a high degree of crystallinity. No other crystalline phases were observed in
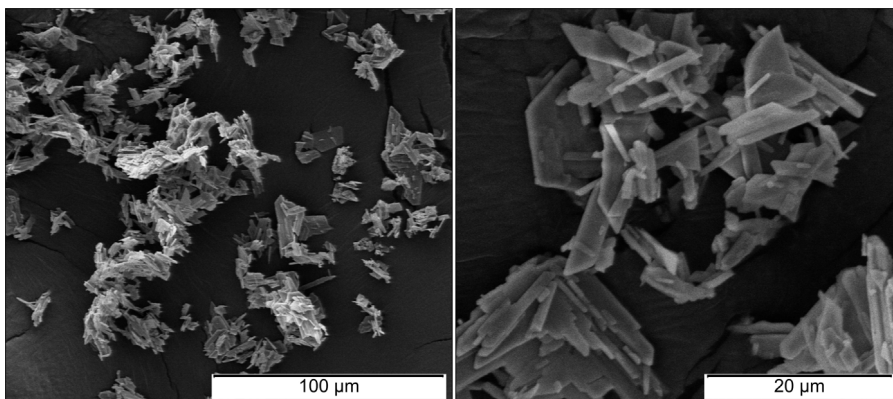
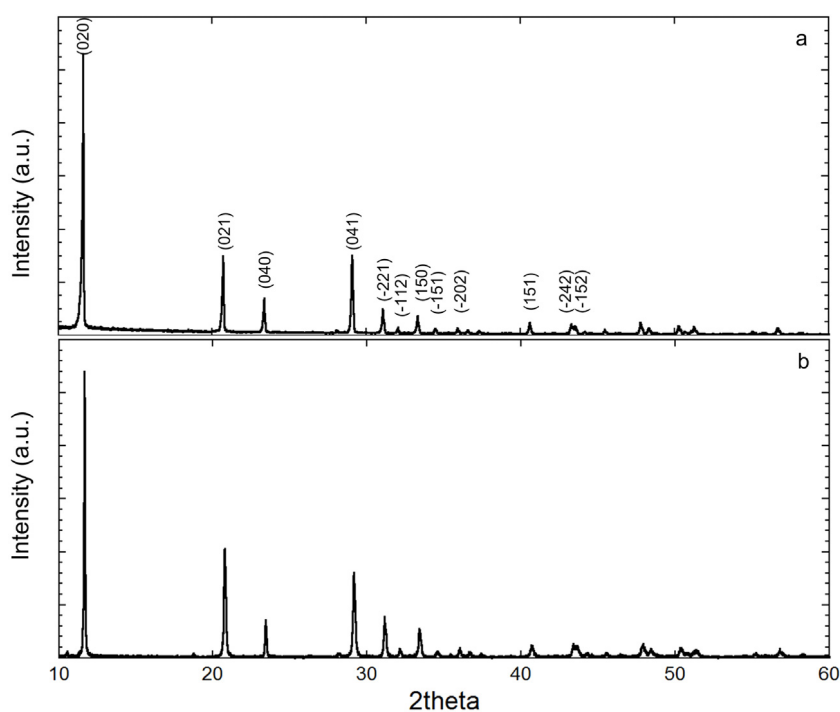**Fig. 1.** SEM images of obtained $CaSO_4 \cdot 2H_2O$ crystals.

Fig. 2. XRD analysis: a – synthetic gypsum; b – natural gypsum powder for comparison (Anon, 2019a).

the diffractograms (see Fig. 2). Calculated average grain size values of the samples were 82 nm (calculated for the peak at 11.61 degrees 2theta). The impurities contained in the chalk (clay minerals, quartz) were not found in the composition of the resulting cake — precipitates of calcium sulphate dehydrate. Accordingly, they remained in the bittern and were removed during the phase of filtration.

Effective removal of impurities from the precipitate suggests that they were not co-crystallized in the structure of $CaSO_4 \cdot 2H_2O$, but sorbed on the surface of the crystals.

The d-spacing values of 3.07, 2.69 and 2.09 Å shown in Fig. 3 fully correspond to the peaks at 29.1, 33.3 and 43.3 degrees 2theta in XRD (Fig. 3). The found beta angles of 122.8° and 112.6° are quite different from the standard value of 118.43°. Instead, they seem closer to another reference XRD spectrum of gypsum m with space group C2/c and beta $\sim$ 127°, and a further C2/c setting with a $\sim$6.27, b $\sim$15.20, c $\sim$5.67 Å, beta $\sim$114° (Anon, 2019b).

Fig. 4 shows the dependence of the mass change on the production temperature of the material obtained.

On stage I from 0 °C to 103 °C, residual physical moisture is removed and resulted in a weight change of 0.39 wt.%. The endothermic effect associated with the removal of water of crystallization is recorded at stage II in the range of 103–175 °C. At 103 °C the separation of 1.5 H_2O molecules begins with the formation of $CaSO_4 \cdot 0.5H_2O$. After that,
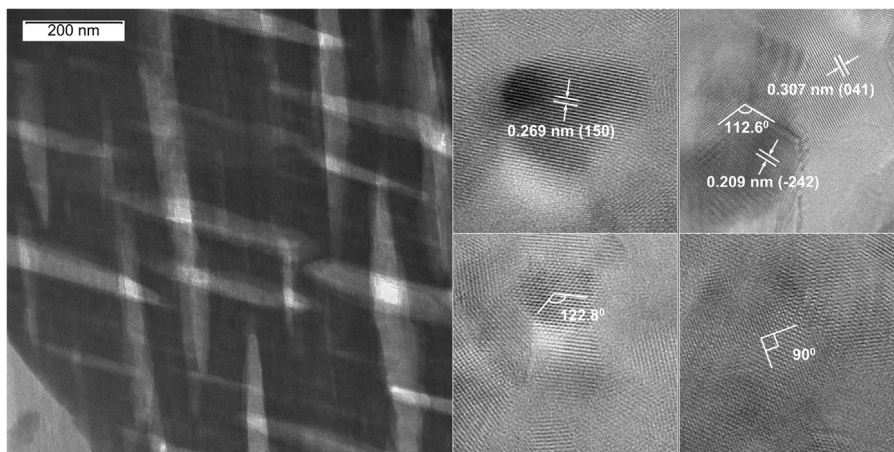
Fig. 3. High resolution TEM image of synthetic gypsum. Single grains, atomic distances and angles in grains are also shown.
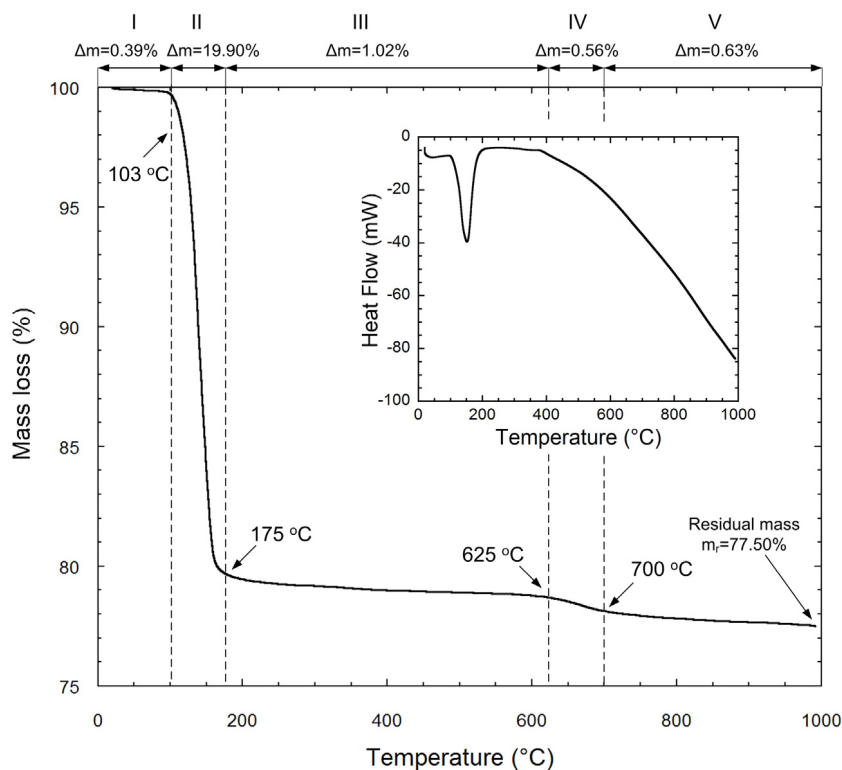

Fig. 4. The dependence of the change in the mass of synthetic gypsum, obtained by sulphuric acid decomposition of chalk, as a function of temperature.

the remaining 0.5 molecules of crystallized water begin to separate, with further production of $CaSO_4$. The dehydration process is completed when the temperature reaches 175 °C, and this leads to 19.90 wt.% of sample mass loss. It should be noted that the temperature of these endo-effects is 15–20 °C lower than that of natural gypsum (Luo et al., 2010). This can be explained by the greater dispersion of synthetic gypsum, as well as by the presence of mineral impurities in it, which affect the topochemical mechanism of dehydration of $CaSO_4 \cdot 2H_2O$.

At stage III in the temperature range of 175–625 °C, the process of splitting off the remaining crystallized water is completed and soluble anhydrite is obtained. This caused a 1.02 wt.% mass loss.

At stage IV, a diffuse relatively shallow endothermic effect is recorded at 625–700 °C corresponding to the beginning of the decomposition of carbonate-containing compounds, i.e. impurities of magnesium carbonate, which is a rest component of chalk. This corresponds to a mass loss of 0.56 wt.%.

On stage V, the decomposition of relict carbonates of Ca and Mg is completed. Observed mass loss was 0.63 wt.%.

According to the TGA data it can also be concluded that the obtained material is $CaSO_4 \cdot 2H_2O$.

To the best of the knowledge of the authors, nobody was so far engaged in targeting production of synthetic calcium sulphate dihydrate on an industrial scale, since there are large reserves of natural gypsum stone. However, there are a number of countries that lack their own gypsum deposits but have deposits of calcium carbonate and chemical productions that produce or use sulphuric acid. These studies have proven the possibility of purposeful production of calcium sulphate dihydrate from carbonate raw materials and sulphuric acid. It was even more importantly proven that production waste can be successfully used in this synthesis, by using spent sulphuric acid from the production of chemical fibres and screening fines limestone, which is formed in sugar and steel mills with the production of lime in shaft furnaces. The use of synthetic gypsum can hence be used for recycling of industrial waste.

4. Conclusions

The following main conclusions were drawn:

1. Analysis of the parameters for the synthesis of calcium sulphate dihydrate derived from local carbonate raw materials (chalk) and spent sulphuric acid suggests that this process was feasible to obtain the target product at a given quality.

2. A larger number of big crystals of the prismatic form $CaSO_4 \cdot 2H_2O$ were formed, which facilitated the filtration stage and increased the strength characteristics of gypsum binders.

3. The developed cycle for producing synthetic calcium sulphate dihydrate is a closed water cycle, i.e. all the separated water in the centrifuging process is used for preparing the chalk suspension at the subsequent first stage of production.

4. The structure-controlled synthesis of calcium sulphate dihydrate made it possible to obtain particles of 200–500 μm in size, which greatly simplified the process of separating obtained gypsum from the mother liquor and allowed to separate at least 95 wt.% of crystals formed by centrifugation. The remaining crystals in the mother liquor can be used as seed for the next synthesis cycle.

5. Impurities introduced together with the raw material were effectively removed from the resulting precipitate by washing. This indicates that they are not co-crystallized in the structure of $CaSO_4 \cdot 2H_2O$, but was sorbed on the surface of the crystals.

6. The resulting synthetic gypsum prepared by optimal parameters contained not less than 95 wt.% of calcium sulphate dihydrate, which corresponds to the natural gypsum stone grade I (Anon, 2008).

Author contributions

M.K. performed lab experiments. M.K. and V.R. performed an analysis of the synthesized product. The methodology of the synthesis was proofed by M.K. and N.K. W.K. helped with different resources for analysis of the synthesized product. All figures were prepared by V.R. M.K. and V.R. prepared the initial draft of the manuscript. All authors analyzed the data, contributed to a discussion of the results, provided inputs on the main manuscript text and approved the final version. V.R. was responsible for poof original draft, submitting, review and editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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