

Influence of Ce^{3+} on the Formation of α -Semi-Hydrate Gypsum

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Influence of Ce^{3+} on the formation of α -semi-hydrate gypsum was investigated in this work. α -semi-hydrate gypsum is normally obtained by heat conversion of the dihydrate gypsum. The model system: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was designed. The amount of $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ corresponding to 0.1; 0.5 and 1 % of Ce_2O_3 from the mass of dry materials (gypsum) was added to solution. Maleic anhydride ($\text{C}_4\text{H}_2\text{O}_3$) was used as crystal modifier and 0.1 % of $\text{C}_4\text{H}_2\text{O}_3$ from the mass of dry materials (gypsum) was added to solution. Water/gypsum of the suspension was equal to 2. The system was processed under hydrothermal conditions at $128 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ and $138 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ temperature; the duration of isothermal curing was 3 hours. The product obtained was treated at $400 \text{ }^\circ\text{C}$ temperature. The X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FT-IR) scanning electron microscopy (SEM) was used to characterize the product.

The results showed that the larger amount of Ce^{3+} in the system, the larger the remaining amount of un-dehydrated dihydrate gypsum in the final product, and the resulting crystals of α -semi-hydrate gypsum are tiny, indefinite and irregular in shape. Therefore, the results obtained lead to a conclusion that Ce^{3+} has a negative influence on the dehydration of dihydrate gypsum (or on the formation of α -semi-hydrate gypsum) and the morphology of α -semi-hydrate gypsum crystals.

Keywords: gypsum, α -semi-hydrate gypsum, cerium sulphate octahydrate, dehydration, crystal morphology.

1. INTRODUCTION

Natural dihydrate gypsum is the main raw material for the production of gypsum binding materials. Lithuania has no deposits of natural dihydrate gypsum that could be used to make gypsum binding materials. It could be replaced by the technological waste containing calcium sulphate, for instance, phosphogypsum [1–6], which forms in the phosphoric acid production process by decomposing phosphate rock with sulphuric acid and phosphoric acid. Depending on technological parameters, the process results in dihydrate phosphogypsum or semi-hydrate phosphogypsum.

Due to a relatively large amount of phosphate impurities, phosphogypsum is not widely used in the industry of construction materials. The morphology and size of crystals of phosphogypsum have influence on the amount of water-soluble phosphate impurities in it. It is known that crystal morphology depends on the impurities contained in phosphate rock [7].

Previous research [8] has proven that the semi-hydrate phosphogypsum obtained from Kovdor and Kirovsk apatites differs in crystal morphology and physical-mechanical properties. The phosphate rock of the aforementioned localities does not only differ in the amount of the main components CaO , P_2O_5 and F but also other components, in particular the amounts of MgO , Al_2O_3 and Ln_2O_3 (Ce_2O_3 , La_2O_3).

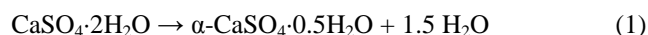
Scientific data on the influence of Mg^{2+} , Al^{3+} , F^- and other ions in phosphate rock on crystal morphology and a particle size of dihydrate phosphogypsum formed in the production of phosphoric acid are not comprehensive and

often contradictory [7, 9–15], whereas the influence of Ln^{3+} on the crystal morphology of dihydrate phosphogypsum has been little studied [15–17].

The influence of impurities contained in phosphate rock on the crystal morphology of semi-hydrate phosphogypsum has been unspecified so far [13].

Since the semi-hydrate phosphogypsum under analysis is a multi-component compound, it is rather difficult to evaluate the influence of impurities on the crystal morphology of semi-hydrate phosphogypsum. It is appropriate to form model systems in order to dissociate from other compounds (impurities) and to determine the influence of Al^{3+} , Mg^{2+} , F^- and other impurities containing Ln^{3+} , Fe^{3+} and Na^+ on the crystal morphology of semi-hydrate gypsum. The determination of the impact of the above-mentioned ions on the properties of semi-hydrate gypsum will lead to a more accurate evaluation of their influence on the properties of semi-hydrate phosphogypsum.

Semi-hydrate gypsum ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) is usually obtained from dihydrate gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). When dihydrate gypsum is treated in the saturated vapour at $120 \text{ }^\circ\text{C}$ and pressure 0.13 MPa, it results in a loss of hydration water (H_2O) [18]. The dehydration of dihydrate gypsum to α -semi-hydrate gypsum occurs according to the reaction [19]:



Previous studies [20] relied on model systems ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{NaF}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{Na}_2\text{SO}_4$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$), by adding such amounts of soluble salts into the systems that the concentration of Al_2O_3 , Fe_2O_3 , MgO , Na_2O , F would equal to 0.1 % – 2 % and it would be close to their amount in phosphate rock.

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Maleic anhydride ($C_4H_2O_3$) was used as crystal modifier and 0.1 % of $C_4H_2O_3$ from the mass of dry materials (gypsum) was added to solution. The results revealed that when the systems containing Al^{3+} , Mg^{2+} , F^- [20] as well as Fe^{3+} and Na^+ in addition to dihydrate gypsum are processed under hydrothermal conditions at 128 °C temperature, the duration of isothermal curing – 3 hours and the product obtained is subsequently treated at 400 °C temperature, the final product is α -semi-hydrate gypsum differing in crystal morphology.

The aim of this study is to determine the influence of cerium ions on the formation of α -semi-hydrate gypsum.

2. EXPERIMENTAL DETAILS

Reagents: gypsum $CaSO_4 \cdot 2H_2O$ (99.97 % purity Sigma-Aldrich, Germany), cerium (III) sulphate octahydrate $Ce_2(SO_4)_3 \cdot 8H_2O$ (≥ 99.9 % purity, Lachema, Czech Republic), maleic anhydride $C_4H_2O_3$ (≥ 99 % purity, Sigma-Aldrich, Germany).

α -semi-hydrate gypsum ($CaSO_4 \cdot 0.5H_2O$) was obtained from gypsum ($CaSO_4 \cdot 2H_2O$) in rotating autoclave “Lampart” at 128 °C \pm 2 °C and 138 °C \pm 2 °C temperature; the duration of isothermal curing was 3 hours. Dehydration of gypsum has been carried out when water/gypsum of the suspension was equal to 2. Maleic anhydride ($C_4H_2O_3$) was used as crystal modifier and 0.1 % of $C_4H_2O_3$ from the mass of dry materials (gypsum) was added to solution [21]. The amount of $Ce_2(SO_4)_3 \cdot 8H_2O$ corresponding to (0.1 – 1) % of Ce_2O_3 from the mass of dry materials (gypsum) was added to solution. The products of the synthesis have been filtrated, rinsed with ethyl alcohol to prevent hydration of materials, dried at 100 °C \pm 2 °C temperature 24 hours.

Ignition loss of semi-hydrate gypsum was determined by heating the substance at 400 °C temperatures.

Scanning electron microscopy (SEM) (OXSFORD ISIS LEO 440i, UK) of the samples was performed using an accelerating voltage of 20 kV and a working distance of 10 mm for SEM observation.

The X-ray powder diffraction (XRD) data were collected with DRON-6 X-ray diffractometer with Bragg-Brentano geometry using Ni-filtered Cu K_α radiation and graphite monochromator, operating with voltage 30 kV and emission current of 20 mA. The step-scan covered the angular range 5°–60° (2θ) in steps of $2\theta = 0.02^\circ$. For diffraction profile refinement under the pseudo Void function and for a description of the diffractional background under the 3rd degree Tchebyshev polynomial, we used a computer program X-fit [22]. The materials were identified using database JCPDS (International Centre for Diffraction Data, Swarthmore, PA).

Fourier-transform infrared spectroscopy (FT-IR) was carried out with the help of spectrometer Perkin Elmer FT-IR system Spectrum GX. Specimens were prepared by mixing 1 mg of the sample in 200 mg of KBr. The spectral analysis was performed in the range (4000 – 400) cm^{-1} with spectral resolution of 1 cm^{-1} .

3. RESULTS AND DISCUSSION

When dihydrate gypsum is processed under hydrothermal conditions at 128 °C \pm 2 °C temperature and

the product obtained is treated at 400 °C temperature, the amount of hydration water in it equals to 6.1 %. In theory, the amount of hydration water in semi-hydrate gypsum amounts to 6.2 % [19].

Therefore, the results obtained lead to a conclusion that the product resulting in the reaction is α -semi-hydrate gypsum.

The X-ray diffraction analysis (Fig. 1, curve 1), showed the diffraction peaks (d – 0.6013; 0.3467; 0.3006; 0.2803; 0.1849; 0.1845 nm) characteristic of semi-hydrate gypsum. Thus, the results confirm that the material formed in the reaction is α -semi-hydrate gypsum.

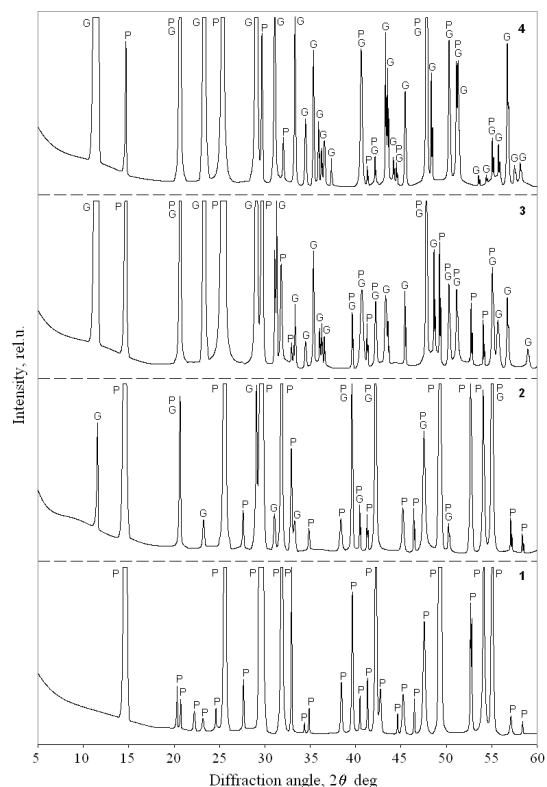


Fig. 1. X-Ray diffraction patterns of product obtained in the systems without and with $Ce_2(SO_4)_3 \cdot 8H_2O$: 1 – without $Ce_2(SO_4)_3 \cdot 8H_2O$, 2 – with $Ce_2(SO_4)_3 \cdot 8H_2O$ (0.1 % Ce_2O_3 in the system), 3 – with $Ce_2(SO_4)_3 \cdot 8H_2O$ (0.5 % Ce_2O_3 in the system), 4 – with $Ce_2(SO_4)_3 \cdot 8H_2O$ (1 % Ce_2O_3 in the system). Indexes: P – semi-hydrate gypsum, G – gypsum

The peaks identified in FT-IR spectrum (Fig. 2, curve 1) are typical of this compound. A group of absorption bands in the (3600 – 3200) cm^{-1} region were referred to valence vibrations of the O-H bond in water molecules. In semi-hydrate gypsum, O-H vibrations can be seen at the range 3610 cm^{-1} and 3550 cm^{-1} . The range of (1620 – 1680) cm^{-1} is assigned to the H–O–H deformation mode. A single absorption band with a maximum at 1620 cm^{-1} is typical for semi-hydrate gypsum [23]. Absorption bands at 1146, 995 cm^{-1} are attributed to valence vibrations of oxygen atoms in sulphate group. The bands at 660 cm^{-1} and 600 cm^{-1} are assigned to the deformation vibrations of oxygen atoms in sulphate group [24].

The SEM images (Fig. 3) of α -semi-hydrate gypsum showed the prevalence of hexagonal prism-shaped crystals characteristic of α -semi-hydrate gypsum [25].

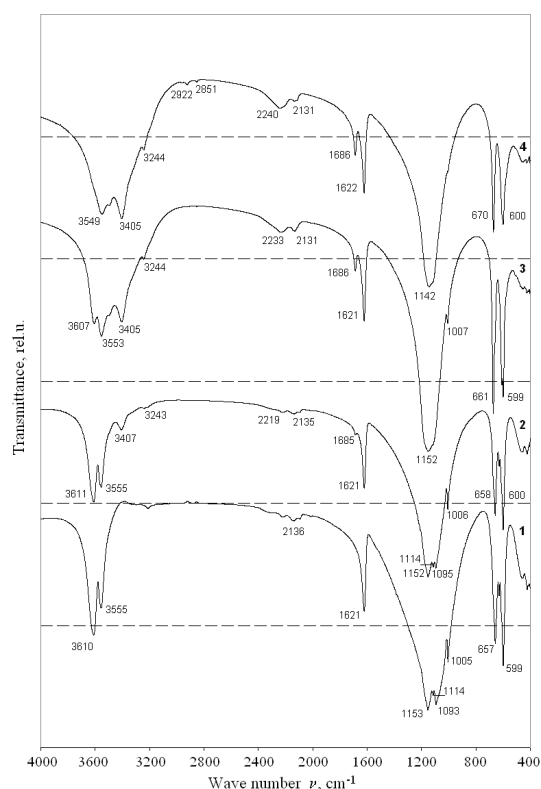


Fig. 2. FT-IR spectrum of product obtained in the systems without and with $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$. 1 – without $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, 2 – with $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (0.1 % Ce_2O_3 in the system), 3 – with $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (0.5 % Ce_2O_3 in the system), 4 – with $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ (1 % Ce_2O_3 in the system)

When $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is processed with $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ admixture (Ce_2O_3 0.1 % – 1 %) under hydrothermal conditions at $128^\circ\text{C} \pm 2^\circ\text{C}$ temperature and the product obtained is treated at 400°C temperature, it contains a large amount of hydration water (Table 1).

The results show that the larger amount of Ce^{3+} in the system, the more hydration water is in the final product. It is an indication that gypsum dehydrated incompletely.

The data received supports from the X-ray diffraction analysis results (Fig. 1, curves 2–4), showing that the larger the amount of Ce^{3+} , the higher the intensity of diffraction maximums ($d = 0.7601, 0.4281, 0.3064, 0.2872$ and 0.2686 nm) typical of dihydrate gypsum.

The analysis of FT-IR spectrum (Fig. 2, curves 2–4) revealed the difference (form, intensity) in the type of

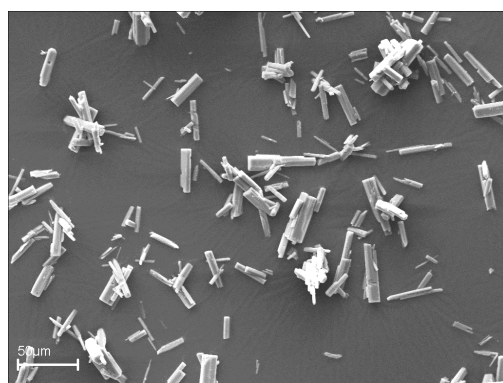


Fig. 3. SEM images of α -semi-hydrate gypsum

absorption bands ($3600 - 3200 \text{ cm}^{-1}$ and $1620 - 1680 \text{ cm}^{-1}$) depending on the change in the amount of hydration water.

Table 1. Amount of hydration water in the product dependence on the amount of Ce_2O_3 in the system

Ce_2O_3 , %	Amount of hydration water, %	
	hydrothermal conditions at $128^\circ\text{C} \pm 2^\circ\text{C}$ temperature	hydrothermal conditions at $138^\circ\text{C} \pm 2^\circ\text{C}$ temperature
0.1	8.24	6.93
0.5	11.42	8.72
1.0	17.75	16.09

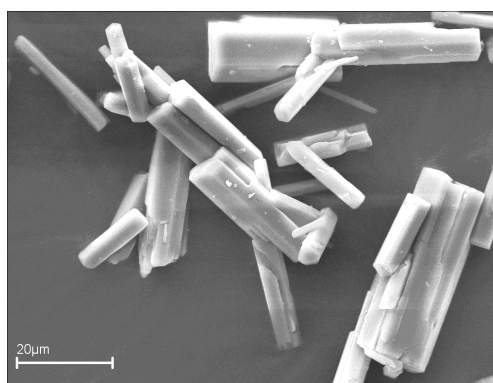
The valence vibrations of the OH-bond of water molecules in semi-hydrate gypsum can be seen at 3610 and 3550 cm^{-1} , whereas in dihydrate gypsum they shift to the shorter waves (3540 and 3400 cm^{-1}). The range of ($1620 - 1680 \text{ cm}^{-1}$) is assigned to the H–O–H deformation vibrations. Semi-hydrate gypsum can be characterised by a single absorption band at 1620 cm^{-1} , whereas dihydrate gypsum exhibits two bands (1680 and 1620 cm^{-1}) [23].

As the amount of Ce^{3+} in the system increases, absorption bands at the range of $3600 - 3200 \text{ cm}^{-1}$ become broader and shift to the side of shorter waves, while the band at 1680 cm^{-1} gets more intensive. It confirms the presence of a larger amount of water in the resulting product structure.

When the temperature of hydrothermal treatment is increased to $138^\circ\text{C} \pm 2^\circ\text{C}$, the dehydration of dihydrate gypsum in the system $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ accelerates as the amount of hydration water decreases (Table 1). However, the products obtained still contain a large amount of dihydrate gypsum. It means that Ce^{3+} has a greater influence on the resulting compound than the increase in temperature.

SEM analysis of the products obtained under hydrothermal conditions at 128°C was carried out (Figs. 4–6). It has been identified that the crystals of the products obtained from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ admixture differ from the crystals of the α -semi-hydrate gypsum (product obtained from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ without $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ admixture (Fig. 3).

SEM images (Fig. 4) of the material with a small amount of Ce^{3+} (the admixture contains 0.1 % Ce_2O_3) show the dominance of hexagonal prism-shaped crystals but tiny crystals of indefinite, irregular shape can also be found.



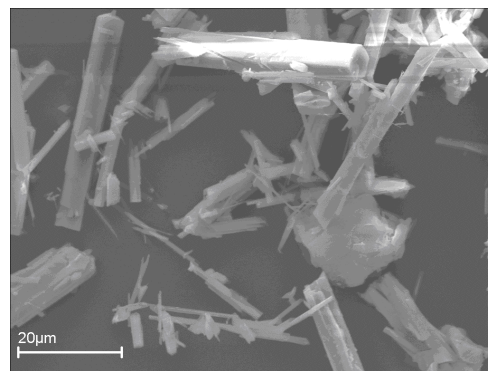
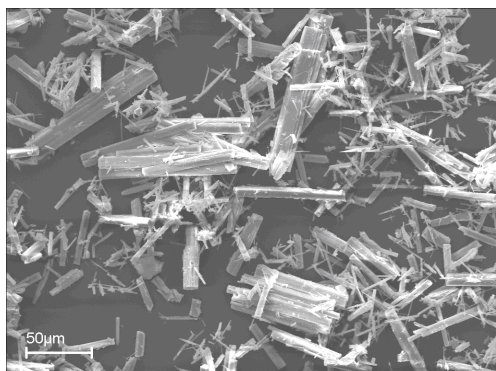


Fig. 4. SEM images of product obtained from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with $\text{Ce}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ ($\text{Ce}_2\text{O}_3 - 0.1\%$)

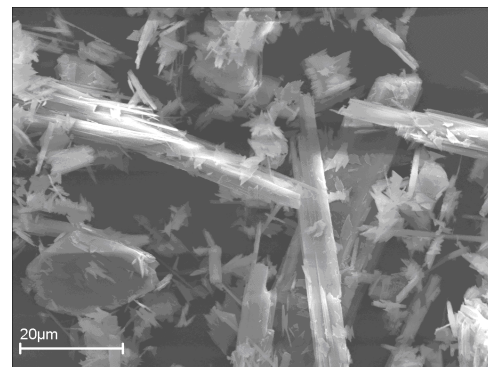
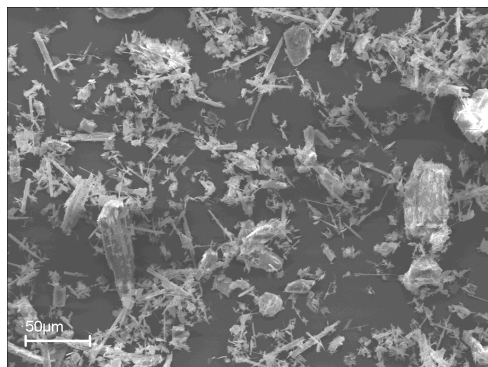


Fig. 5. SEM images of product obtained from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with $\text{Ce}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ ($\text{Ce}_2\text{O}_3 - 0.5\%$)

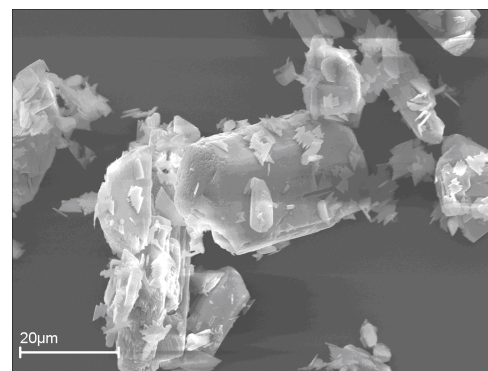
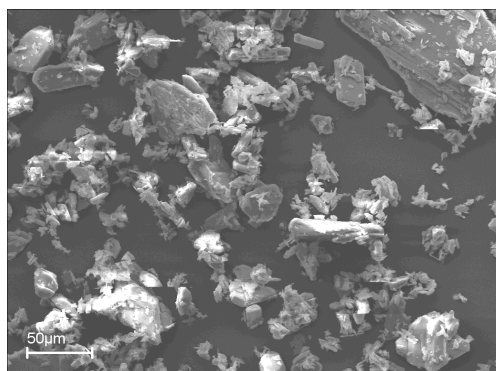


Fig. 6. SEM images of product obtained from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ with $\text{Ce}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ ($\text{Ce}_2\text{O}_3 - 1\%$)

When the amount of Ce^{3+} in the system is increased (0.5 % Ce_2O_3), the SEM images (Fig. 5) of the final material show the crystals of three-fold morphology: long and thin crystals resembling the crystals of α -semi-hydrate gypsum by their shape; larger crystals characteristic of dihydrate gypsum; and tiny irregular-shaped crystals.

Large crystals typical of dihydrate gypsum prevail amidst the crystals of the product obtained in the system with a large amount of $\text{Ce}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ (1 % Ce_2O_3) (Fig. 6). The data supports the results of X-ray diffraction and FT-IR analyses showing large amounts of un-dehydrated dihydrate gypsum in the material.

The results show that even a small amount of this admixture (0.1 % Ce_2O_3) has influence on the crystal morphology.

Hence, it can be concluded that with Ce^{3+} in the system, not only is the full dehydration of dihydrate gypsum prevented but the resulting crystals of α -semi-hydrate gypsum are tiny, indefinite and irregular in shape.

To find out why α -semi-hydrate gypsum fails to form in the system $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ in the course of hydrothermal processing, the reaction of $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ with the crystallization regulator – maleic anhydride ($\text{C}_4\text{H}_2\text{O}_3$) was carried out. The process resulted in gel deposits. It is known that complex compounds form in the reaction between lanthanoids and organic compounds [26]. Hence, it may be assumed that $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ reacted with $\text{C}_4\text{H}_2\text{O}_3$, and the gel deposits are their complex compound.

It is likely that when $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is processed with $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ admixture under hydrothermal conditions, $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ also reacts with $\text{C}_4\text{H}_2\text{O}_3$, thus resulting in their complex compound. The larger the amount of Ce^{3+} in the system, the larger share of complex compound is obtained, whereas the final product retains a higher amount of un-dehydrated dihydrate gypsum. Therefore, it may be supposed that the complex compound of $\text{Ce}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $\text{C}_4\text{H}_2\text{O}_3$ envelopes the crystals of dihydrate gypsum,

thus preventing them from dehydration (slowing down their dehydration).

Furthermore, the experiment revealed that with a larger amount of Ce^{3+} in the system, the reaction results in a denser suspension which is more difficult to filtrate. Such a phenomenon can be observed when a crystallisation regulator is not used [21].

Thus, it is likely that due to the formation of the $Ce_2(SO_4)_3 \cdot 8H_2O$ and $C_4H_2O_3$ complex, $C_4H_2O_3$ loses its crystallisation regulator's function. This fact is also supported by the SEM analysis (Figs. 4–6), which shows that with the growing amount of Ce^{3+} in the mixture, the number of tiny crystals of indefinite and irregular shape increases.

4. CONCLUSIONS

It has been determined that Ce^{3+} has a negative influence on the dehydration of dihydrate gypsum (or on the formation of α -semi-hydrate gypsum) and the morphology of α -semi-hydrate gypsum crystals, when dihydrate gypsum is treated with $Ce_2(SO_4)_3 \cdot 8H_2O$ admixture for 3 hours under hydrothermal conditions at $128 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ temperature. The larger amount of Ce^{3+} in the system, the larger the remaining amount of un-dehydrated dihydrate gypsum in the final product (or the smaller amount of α -semi-hydrate gypsum is in the final product), and the resulting crystals of α -semi-hydrate gypsum are tiny, indefinite and irregular in shape.

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