# THE INFLUENCE OF MAGNESIUM CHLORIDE CONCENTRATION IN THE LIQUID PHASE ON THE HYDROTHERMAL DEHYDRATION OF GYPSUM

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The thermal treatment of gypsum in boiling 1M, 2M, 3M, 4M and 4,5M solutions of magnesium chloride, at atmoshperic pressure, in order to obtain  $\alpha$ -CaSO<sub>4</sub>.0,5H<sub>2</sub>O was performed. Three mechanism of  $\alpha$ -hemihydrate formation were identified in solutions of different concentrations. Gypsum transformation into  $\alpha$ -hemihydrate operated in solid phase, through an intermediate product,  $\beta$ -hemihydrate, in solutions of low concentrations (1 and 2M), direct in solutions of high concentrations (3 and 4M) and in solid phase in the solution of the highest concentration (4,5M). Specific surface areas of the obtained products indicated that slow transformation processes (regardless of the mechanism involved) gave products of small surface areas, or high usability.

## INTRODUCTION

Calcium-sulphate hemihydrate is an intermediate product of dihydrate dehydration reaction; it occurs in two, crystallographically identical, forms:  $\alpha$  and  $\beta$ , the former having a better ordered crystal lattice than the latter /1/. The two forms are composed of particles of different characters:  $\alpha$  of smooth, clear and transparent, regular (needle-like, prismatic, rod-like) crystals, and  $\beta$  of white, porous, soft, irregular particles of large specific surface areas. Particle surface areas are the most important quality of the hemihydrate. The form with particles of small surface areas, when used, links a smaller amount of water and gives a product of better mechanical properties - the hard or superhard gypsum, unlike the other form  $(\beta)$ , which links more water and gives a less good product the white gypsum /2/.

Different forms of the hemihydrate are products of different technologies:  $\beta$  is a product of dry /13/, and  $\alpha$  of wet treatments. In a dry treatment, water from dihydrate interfaces diffuses as vapour through the hemihydrate, significantly disturbing the crystal lattice structure, forming an incoherent granular structure of rough surfaces and large surface areas. This product is referred to as  $\beta$ -hemihydrate.

The dehydration reaction in a wet treatment is more complex than in a dry treatment, due to the liquid phase. The properties of the liquid phase have a significant effect on the dehydration reaction and its time and consequently the quality of the product /10, 11, 12/. The wet dehydration reaction mechanisms, and the effects of the liquid medium have not been adequately studied and reported. There are even controversial statements in literature. Some authors state that the reaction in these processes occur only in the solid phase (water molecules in the form of drops are slowly diffused through the hemihydrate, slightly disturbing the crystal lattice structure) or only in the solution (dihydrate dissolves and hemihydrate crystals grow from the solution (6, 9) or simultaneously in either phase /4, 5, 11/.

In an earlier experiment, we discovered that  $\alpha$ hemihydrate, under the hydrothermal treatment, could be formed also from the intermediate product of  $\beta$ -hemihydrate which, dissolved, formed a saturated solution that gave rise to the  $\alpha$ -hemihydrate crystal growth /3/.

We report here the concentration effect of the liquid phase, in which the mineral was thermally treated, on the reaction of gypsum hydrothermal dehydration. The concentration of the liquid phase was varied using  $MgCl_2$  salt, while all other experimental conditions were the same.

# EXPERIMENTAL

Gypsum was analysed by the conventional chemical method, qualitative IR and X-ray examinations for extablishing its chemical composition and purity. For the qualitative IR and X-ray examinations, PERKIN-ELMER spectrometer type 397 and X-ray diffractometer PHILIPS 990301/05 were used, respectively.

Ten grams of the mineral (grain size -0.174 + 0.074 mm) were boiled in 100 cm<sup>3</sup> MgCl<sub>2</sub> aqueous solution of different concentraions: 1; 2; 3; 4 and 4,5M at respective boiling temperatures of the solutions and atmospheric pressure. The mineral was boiled until the desired  $\alpha$ -hemihydrate has been formed.

A charge reactor was used for all experiments with ideal stirring rate (n = 400 rpm). After having boiled for a predetermined time, products were separated from the liquid phase by vacuum filtration and rinsed under boiling distilled water until the reactions with  $Mg^{2+}$  and  $Cl^-$  ions have become negative.

Rinsed products were over-dried at 100° C and subjected to microscopy and qualitative IR analysis for determining the composition.

Chemical composition of gypsum									
Material	H <sub>2</sub> O combined	CaO	$SO_3$	SO <sub>3</sub> /CaO ratio	MgO	Purity			
gypsum Pure dihydrate	20.75 20.93	32.47 32.56	46.54 46.51	1.43 1.43	0.03	99.87 100			

Table I.



Fig. 1. IR spectrum of gypsum.

The products obtained in the above described manner were examined by IR and microscopic analysis in order to establish the reaction mechanism and the period of complete dihydrate transformation into  $\alpha$ hemihydrate.

Dehydration was established when peaks typical of dihydrate presence disappeared (at 3.400 cm<sup>-1</sup> and 1.680 cm<sup>-1</sup>) and peak typical of hemihydrate presence appeared (at 3.600 cm<sup>-1</sup>) in IR spectra /7/.

Formation of calcium sulphate  $\alpha$ -hemihydrate was observed by microscopy and the time of formation  $(t_{\alpha})$  was measured for calculation of the velocity of dihydrate transformation into  $\alpha$ -hemihydrate ( $v = 1/t_{\alpha}$ ). The microscopy used was American Optical Stereoscope Zoom Microscope.

Pure  $\alpha$ -hemihydrate formation was verified in DTA analysis, which showed the presence of the endothermic peaks at  $t > 2.00^{\circ}$  C typical of  $\alpha$  – form hemihydrate (for  $\beta$ -form the peak is at 170° C /1, 9/. Chevenard Joimer Instrument A.D.A.M.E.L, was used for DTA analysis.

Specific surface area, for  $\alpha$ -hemihydrate directly upon transforamtions, was determined by BET method using Flowsorb II 2,300 instrument.

#### **RESULT AND DISCUSSION**

The results of the conventional chemical analysis of gypsum are given in Table I. Infrared spectra and X-ray photographs of gypsum are shown in Figs. 1 and 2. Chemical analysis and interpretations of infrared spectra and X-ray graphs in reference literature /7, 9/ suggest that gypsum used in the experiment, was a pure substance.

The examination results of the products (formed before, at the time and after the completion of dihydrate transformation into hemihydrate) are given in Table II.

Data given in Table II show that the dihydrate dehydration reaction, when solution of the lowest concentration (1M) was used, operated in solid phase giving  $\beta$ -hemihydrate as an intermediate product. Further operation of the process (heating the product) led to  $\beta$ -hemihydrate dissociation and Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>ions passing into the solution. When the solution became saturated,  $\alpha$ -CaSO<sub>4</sub>.0.5H<sub>2</sub>O crystals separated from the solution ( $\beta$ - is more soluble than  $\alpha$ -hemihydrate).

The above description of the  $\alpha$ -hemihydrate formation from gypsum using the solution of concentration



Fig. 2. X-ray photograph of gypsum.

1M can be written as follows:

$$CaSO_4 \cdot 2H_2O(s) \rightarrow \beta - CaSO_4 \cdot 0.5H_2O(s) + (1)$$

$$+ 1.5H_2O(1)$$

$$\beta - CaSO_4 \cdot 0.5H_2O(s) \rightleftharpoons CaSO_4(aq) + 0.5H_2O(1)$$

$$CaSO_4(aq) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$$

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \rightarrow \alpha - CaSO_4 \cdot 0.5H_2O(aq)$$

$$\alpha - CaSO_4 \cdot 0.5H_2O(aq) \rightleftharpoons \alpha - CaSO_4 \cdot 0.5H_2O(s)$$

The appearances of  $\beta$  and  $\alpha$  hemihydrates, obtained using solution of concentration 1M are shown in Figs. 3 and 4.

With the increasing concentration of the solution for thermal treatment the reaction still operates largely in the solid phase and only partly in the solution:

$$CaSO_4 \cdot 2H_2O(s) \rightleftharpoons CaSO_4(aq) + 2H_2O(1)$$
(2)  

$$CaSO_4(aq) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq)$$
  

$$Ca^{2+}(aq) + SO_4^{2-}(aq) + 0.5H_2O(1) \rightleftharpoons$$
  

$$\rightleftharpoons \alpha - CaSO_4 \cdot 0.5H_2O(s)$$

With the solution of a higher concentrations for thermal treatment of the mineral, the reaction operated in the solution (experiments 3, 4). The highest reaction velocity was noted when solution of concentration 3M was used (the product similar in appearance, only of slightly finer grains than that of the preceding experiment – Fig. 6). A further increase in concentration of the solution led to a slower reaction (experiments 4 and Fig. 5). Products of the slower reaction in the solution were smooth, compact, rod-like microcrystals (Fig. 7).

With the solution of the highest concentration for the thermal treatment of the mineral, the reaction operated in the solid phase:

$$CaSO_4 \cdot 2H_2O(s) \rightarrow \alpha - CaSO_4 \cdot 0.5H_2O(s) +$$

$$+ 1.5H_2O(1)$$
(3)

Product of this reaction is  $\alpha$ -hemihydrate composed of particles consisted of smooth, clear and transparent needle like microcristals (Fig. 8).



Fig. 5. Rate of gypsum transformation into  $\alpha$ -hemihydrate and its surface areas (directly upon transformation) versus  $MgCl_2$  solution concentrations.

Different mechanisms of the reactions, and their different rates (Fig. 5), can be explained by the presence of ions of different activities in the solutions: ions of higher activity which break the dihydrate crystal lattice (reaction in the solution) or ions of lower activity which are not capable of affecting it (reaction in solid phase). A slower dehydration, established when a solution of the higher concentration was used, also can be explained by a reduced ionic activity due to the formation of large charaged or uncharged, which are less mobile particles composed of ions. The formation of fine-grained products (microcrystals) can be explained by more than one centre of crystallization in the solutions.

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Mechanism of gypsum transformation into  $\alpha$ -hemihydrate and concentrations of solution

	MgCl <sub>2</sub> solution concentration and boiling	Product compositio gypsum transforma	probable gypsum transformation mechanism		
	points	Before transformation	At transform. completion	Upon transformation and appearance of hemihydr.	
1	1M; 101°C	eta-hemihydrate + gypsum	eta-hemihydrate*	$\alpha$ -hemihydrate composed of long, smooth, needle-like, clear and transparent monocrystals	Reaction in solid phase with $\beta$ -hemihydrate as intermediate product
2	2M; 102°C	$\beta$ -hemihydrate + low $\alpha$ -hemihydr. + gypsam	eta-hemihydrate + small amount of lpha-hemihydrate	$\alpha$ -hemihydrate similar with that in Exp. 1	Same as in Exp. 1 plus small reaction in the solution
3	3M; 109°C	α-hemihydrate + gyfsum	$\alpha$ -hemihydrate	$\alpha$ -hemihydrate similar only finer-grained than in Exp. 1 and 2	Reaction in the solution
4	4M; 124°C	a-hemihydrate + gypsum	α-hemihydrate	$\alpha$ -hemihydrate composed of smooth, clear and transpar- ent rod-like microcrystals	Reaction in the solution
C 4	4,5M; 123°C	a-hemihydrate + gypsun	α-hemihydr <b>ate</b>	$\alpha$ -hemihydrate composed of particles consisted of smooth, clear and transpar- ent needle like microcrys- tals, **	Reaction in the solid phase

\*  $\beta$ -hemihydrate composed of white, porous unclear and untransparent irregular particles (similar shaped as particles of mineral)

\*\* Particles are similar shaped as particles of gypsum.

The reulsts also show that the products, obtained when using solutions of different concentration, are different in appearance and have different surface arreas (Fig. 5) which define their usability; in terms of quality, the best are products of slow dehydration reactions, by both reaction mechanisms, or that the increasing speed of the reaction has an adverse effect on the product quality.

# CONCLUSION

Our experiment data allowed the identification of concentration effects of the magnesium-chloride solution on the mechanism and kinetics of gypsum transformation into  $\alpha$ -hemihydrate and on the properties of this product. The reaction was provoked by a thermal treatment of gypsum mineral in boiling solutions of this salt at atmospheric pressure (hydrothermal process) and the reaction was found to had operated:

- by different mechanisms: in solid or dominantly solid phase forming an intermediate product,  $\beta$ hemihydrate, when solutions of low concentration (1 and 2M) were used, in solution when solutions with high concentrations (3 and 4M) were used or in the solid phase when solution with highes concentrations was used (4,5M);
- at different rates: slow in solutions of the lowest and the highest concentrations (1 and 4,5M), and fast in solutions of medium concentrations (2,3 and 4M).
- forming α-hemihydrate of different surface areas; product of a smaller surface area and better us-

ability was obtained at slow transformation rates (1 and 4,5M) and larger one at fast rates (2,3 and 4M);

• in an optimum manner form the aspect of the salt consumption for prepartion of the solution for thermal mineral treatment and a good quality of the  $\alpha$ -hemihydrate product in a solution of the lowest concentrations.

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# VLIV KONCENTRACE CHLORIDU HOŘEČNATÉHO VE VODNÉ FÁZI NA HYDROTERMÁLNÍ DEHYDRATACI SÁDROVCE

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Předmětem práce bylo stanovení vlivu koncentrace kapalné fáze při hydrotermální dehydrataci sádrovce na  $\alpha$ hemihydrát. Za tím účelem byl sádrovec zahříván v roztocích MgCl<sub>2</sub> různých koncentrací (1,.2, 3, 4 a 4,5M) při teplotách varu příslušných koncentrací při atmosférickém tlaku. Mikroskopicky, IČ spektrografií a rentgenovou analyzou byl prokázán významný vliv koncentrace příslušné kapalné fáze na rychlost a mechanismus přeměny sádrovce na  $\alpha$ -hemihydrát a na jeho vlastnosti.

V roztocích různých koncentrací byly rozlišeny tři odlišné mechanizmy vzniku  $\alpha$ -hemihydrátu. V roztocích nízké koncentrace (1M a 2M) probíhá přeměna sádrovce na  $\alpha$ -hydrát přes meziprodukt,  $\alpha$ -hemihydrát, ve vysoce koncentrovaných roztocích (3M a 4M) pak přímo, a při nejvyšších koncentracích (4,5M) dochází k dehydrataci v pevné fázi. Zvýšení koncentrace z 1M na 2M a 3M způsobuje progresivní urychlení přeměny sádrovce na  $\alpha$ -hemihydrát. Nejvyšší průměrné rychlosti dehydratace bylo dosaženo v roztoku koncentrace 3M, zatímco další zvyšování koncentrace (na 4M a 4,5M) vedlo k progresivnímu snižování rychlosti přeměny.

Měření specifického povrchu získaných produktů (metodou BET) prokázalo, že pomalé procesy přeměny sádrovce (nezávisle na jejich mechanizmu) poskytují produkty s malým specifickým povrchem, a tedy s lepšími užitnými vlastnostmi.

- Obr. 1. IČ spektrum sádrovce
- Obr. 2. Röntgenogram sádrovce
- Obr. 3. Vzhled β-CaSO<sub>4</sub>.0,5H<sub>2</sub>O získaného z roztoku 1M MaCl<sub>2</sub>
- Obr. 4. Vzhled α-CaSO<sub>4</sub>.0.5H<sub>2</sub> O získaného z roztoku 1M MqCl<sub>2</sub>
- Obr. 5. Rychlost přeměny sádrovce na α-hemihydrát a jeho specifický povrch (ihned po přeměně) v závislosti na koncentraci roztoku MgCl<sub>2</sub>
- Obr. 6. Vzhled α-CaSO<sub>4</sub>.0,5H<sub>2</sub>O získaného z roztoku 3M MgCl<sub>2</sub>
- Obr. 7. Vzhled α-CaSO<sub>4</sub>.0,5H<sub>2</sub>O získaného z roztoku 4M MgCl<sub>2</sub>
- Obr. 8. Vzhled α-CaSO<sub>4</sub>.0,5H<sub>2</sub>O získaného z roztoku 4,5M MgCl<sub>2</sub>





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Fig. 3. Appearance of  $\beta$ -CaSO<sub>4</sub>.O.5H<sub>2</sub>O obtained in 1M MgCl<sub>2</sub> solution.



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Fig. 6. Appearance of  $\alpha$ -CaSO<sub>4</sub>.O.5H<sub>2</sub>O obtained in 3M MgCl<sub>2</sub> solution.



Fig. 4. Appearance of  $\alpha$ -CaSO<sub>4</sub>.O.5H<sub>2</sub>O obtained in 1M MgCl<sub>2</sub> solution.



Fig. 7. Appearance of  $\alpha$ -CaSO<sub>4</sub>.O.5H<sub>2</sub>O obtained in 4M MgCl<sub>2</sub> solution.