

## DEVELOPING A HYDROTHERMAL TECHNIQUE FOR PRODUCTION OF ALPHA-HEMIHYDRATE CALCIUM-SULPHATE FROM FLUE GAS GYPSUM

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*Flue gas gypsum was thermally treated in 3M boiling aqueous solution of sodium-chloride at atmospheric pressure (gypsum-salt solution mixing ratios were: 0.125; 0.25; 0.50; 0.75; and 1.00 g cm<sup>-3</sup>). The results indicated that the gypsum conversion rate increased with the gypsum salt solution mixing ratio and that the products achieved at different rates consisted of crystals varied in morphology, size, and specific surface area; the product of the smallest specific surface area (and the highest usability) was that of the highest gypsum-salt solution mixing ratio. It has also been found that the prolonged thermal treatment, after the hemihydrate has been formed, was without a significant effect on its quality.*

### INTRODUCTION

Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) is a byproduct in a process of phosphoric, boric or some organic (citric, oxalic, tartaric) acid, resulting from the reaction between their calcium salts and sulphuric acid. It is also secondary material in processing some minerals, production of pigments, or some other technological processes. The highest amounts of this gypsum, however, is obtained world-wide in the desulphurization of flue gases, the burning products of different fossil fuels, from large industries [1]. An average production is quoted of 5 tons per 1 ton of sulphur contained in fuel. It is quite certain that more limiting environmental regulations and intensification of industrial development will result in a further and increased processing of this secondary material.

Flue gas desulphurization units, attached to power stations of large industries, operate on their counter-current washing with lime suspension in water; the contact of the gases and water and lime will be successive [2].

Small amounts of this secondary material are used in cement industry, but far the largest quantities are used in the manufacture of gypsum products, primarily beta- and alpha-hemihydrates. Because the particles of this gypsum are very small (20 - 60 μm), they must be agglomerated (usually briquetted) prior to processing for dry production of beta-hemihydrate.

Of particular interest is the use of this gypsum in wet processes for production of alpha-CaSO<sub>4</sub>·0.5H<sub>2</sub>O, which do not require a pretreatment [3]. The

first industries for autoclave production of alpha-CaSO<sub>4</sub>·0.5H<sub>2</sub>O form this material were erected in Germany (Guilini) in 1962 and Japan (Nitto) in 1973 [1].

The latest developed wet technique for production of alpha-hemihydrate is the hydrothermal method based on boiling the raw material in aqueous solution of some salts of acids (with or without surface-active agencies) at atmospheric pressure. This method is presented only in literature and has not yet found its industrial application [3,4]. The reference information indicated that uniform and efficient heat transfer from liquid to solid phase, by this method, provides an economical product of good and uniform quality [5]. Also, as the reaction of hemihydrate formation, according to many authors, operates in a solution [8], this method allows many undesirable constituents to pass into the solution or prevents them entering the products.\*

It follows from the above stated that the new method will be suitable for processing the secondary gypsum, and achievement of desired product quality by selection of respective liquid phase. Consequently, development of this method for processing secondary gypsum from desulphurization of flue gases is technologically and economically feasible.

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\* There are also the opinions in published literature that alpha-CaSO<sub>4</sub>·0.5H<sub>2</sub>O is formed in the solid phase by slow diffusion of water drops from dihydrate interlayers, or simultaneously in the both phases [7].

Published information suggests that if solutions of various salts or acids (with or without surface-active substances) of the boiling points higher than that of water are used, this gypsum would produce large and well developed hemihydrate crystals for preparation of good binder. Hemihydrate crystals can be much influenced by different surface active materials [3,9] to achieve a product of desired properties.

Besides the mentioned operative process parameters of hydrothermal treatment of this gypsum, other parameters, such as gypsum-salt solution mixing ratio and duration of thermal treatment, are reasonably expected to influence the process of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  production and the product properties, but this information is not given in reference literature. The mentioned parameters are certainly extremely important for the economy of an industry-level processing, which was the reason for our attempt to test their influence on hydrothermal production of  $\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ .

#### EXPERIMENTAL PART

Gypsum specimen was subjected to the classical chemical, qualitative IR (Perkin-Elmer spectrophotometer 397) and microscopic (American Optical Stereoscope Zoom Microscope) analyses.

The experiment was performed in laboratory discontinuous reactor with perfect mixing ( $n = 600$  rpm). Different amounts of gypsum was boiled in the same volume of 3M NaCl solution at atmospheric pressure.

The thermally treated hemihydrate was separated from the liquid phase by vacuum filtration, rinsed in boiling water, dried at a temperature of 105 °C, and examined in qualitative IR and microscopic analyses. The time of thermal treatment was prolonged in ten-minute intervals until the final conversion into hemihydrate and beyond it.

The alpha-modification of hemihydrate was confirmed by DTA analysis (Chevenard Joinmer Instrument A.D.A.M.E.L.).

Specific surface areas of the hemihydrate were measured by BET-method (Flowsorb II 2300 unit).

#### RESULTS AND DISCUSSION

Results of classical chemical (table 1) and quantitative IR (figure 1) analyses show chemically pure specimen material with only 2.72 wt. % of impurities. It is an indication that pretreatment is not necessary, but the material can be directly used in the production of alpha-hemihydrate calcium sulphate.

The microscopic analysis of gypsum showed its composition of microcrystal aggregates, irregular and

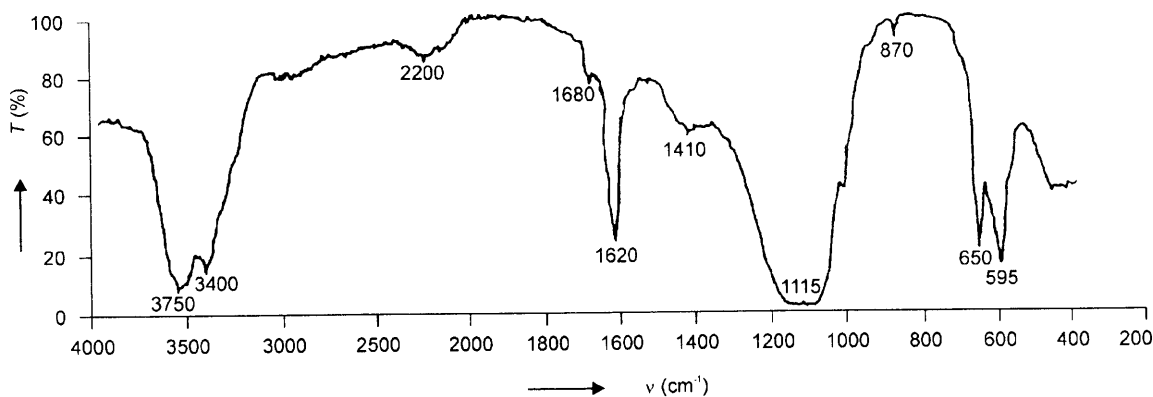


Figure 1. IR spectra of gypsum.

Table 1. Chemical composition of gypsum.

component	CaO	SO <sub>3</sub>	H <sub>2</sub> O	MgO	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
(wt.%)	24.7	55.7	53.26	1.24	0.19	1.29

angular in shape and within a narrow size range (average size 40  $\mu\text{m}$ ) which also suggested its direct use in production of alpha-hemihydrate calcium-sulphate without pretreatment for grain size reduction (grinding) of uniformity (sieving).

The formation of hemihydrate was established from appearance of a IR spectral band at 3600  $\text{cm}^{-1}$ , typical of hemihydrate, or disappearance of bands from 3400 and 1680  $\text{cm}^{-1}$ , typical of dihydrate [9]. The time interval of gypsum conversion  $t_c$  was indicated in the same way and used, with the gypsum mass, to determine the velocity of the conversion of gypsum.

Alpha-hemihydrate modification was verified by DTA, which showed the presence of the endothermic peaks at  $t > 200$  for all hemihydrate samples [11].

The experimental results are given in tables 2 and 3. They show that the velocity of the gypsum conversion increases with the increasing the gypsum-salt solution mixing ratio, and the product obtained at different rates consist of crystals of different properties.

Alpha-hemihydrate calcium-sulphate is composed of large, compact, smooth, clear and transparent monocrystals of the smallest specific area, i.e. best usability, obtained by thermal treatment of gypsum in the highest gypsum-salt solution mixing ratio (exp. no. 4 and 5). Thermally treated gypsum in suspensions of lower gypsum salt solution ratio (exp. no. 1,2,3) gave a product composed of two different crystal forms: (a) monocrystals similar to those in exp. no. 5 and 6, and

(b) angular microcrystal aggregates which seem to give poorer binders.

Table 2. Dependence of gypsum conversion rate on gypsum-salt solution mixing ratio.

gypsum-salt solution mixing ratio (g $\text{cm}^{-3}$ )	gypsum conversion rate (g $\text{min}^{-1}$ )
0.125	1.500
0.250	3.100
0.500	6.000
0.750	12.000
1.000	25.100

The occurrence of crystal conglutination was noted in the densest suspension (exp. no. 5), which is very unfavourable from the crystal utilization aspect [8]. The occurrence can be explained by congestion of hemihydrate crystals preventing their growth. The use of a higher gypsum-salt solution mixing ratio than this would give the product of unsatisfactory quality.

For an assessment of the purposefulness of thermal treating the material (in the highest gypsum-salt solution mixing ratio), surface areas were determined, after dehydration, of hemihydrate crystals for different time intervals (table 4).

Table 3. Properties of hemihydrate crystals produced at different rates, for  $t = t_c$ .

gypsum conversion rate (g $\text{min}^{-1}$ )	$\alpha\text{-CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ crystals morphology	particles average arithmetic length and width ( $\mu\text{m}$ )	particles specific surface ( $\text{m}^2 \text{g}^{-1}$ )
1.500	compact, smooth, clear and transparent monocrystals and ( $\approx 20$ wt.%) angular microcrystal aggregates	32.00 2.00	1.60
3.100	compact, smooth, clear, transparent and translucent monocrystals and ( $\approx 10$ wt.%) smaller angular microcrystals aggregates	37.00 2.60	1.01
6.0	compact, smooth, clear, transparent and translucent monocrystals and ( $\approx 3$ wt.%) the smallest angular microcrystal aggregates	28.00 2.90	0.70
12.0	large, compact, smooth clear and transparent monocrystals and a negligible amount of angular microcrystal aggregates	40.00 3.80	0.42
25.1	large, compact, smooth, clear and transparent monocrystals; the occurrence of crystals conglutination was also noticed	55.00 7.50	0.40

Table 4. Ratio of specific surface areas of alfa-hemihydrate produced in time intervals  $t$  and  $t_c$ .

$t$ (min)	30	35	40	50	60	70	80	90	120	180
$Sp_t/Sp_{td}$	1.01	1.02	1.00	1.01	1.03	1.02	1.01	1.02	1.02	1.01

The achieved results have shown that prolonged thermal treatment, after the gypsum has converted, has not any significant effect on the product quality or economic justification.

The results are not simple to explain, because gypsum was thermally treated in boiling concentrated aqueous solution of sodium-chloride ( $T_k = 107$  °C) in which the interaction of ions is complex and strong. The higher speed of gypsum conversion reaction, in suspensions with higher gypsum-salt solution mixing ratio, may be probably explained by the higher rate of the reaction in the solution provided by higher concentration gradients and interphase areas whose products are monocrystals of the mentioned properties. In suspensions of lower gypsum-salt solution mixing ratio (exp. no. 1,2,3), the reaction in the solution is paralleled with the slower reaction in the solid phase. This hypothesis is supported by the appearance of a portion of the product, composed of microcrystal aggregates similar to raw material particles only finer grained.

### CONCLUSION

It follows from the experimental results reported here that gypsum, as a byproduct of flue gas desulphurization, can be hydrothermally treated (boiled in sodium-chloride solution) to produce a good-quality alpha-hemihydrate calcium sulphate composed of large, smooth, compact, acicular monocrystals. It has been found that:

- There is mutual dependence between the gypsum-salt solution mixing ratio and the rate of gypsum conversion reaction, i.e. the reaction rate is increasing with this ratio.
- Alpha-hemihydrate calcium sulphate, formed at different reaction rates (in suspensions of different mixing ratios), has different specific surface areas and thereby varied utilizations. The best hemihydrate product was obtained at higher mixing ratios (1 or  $0.75 \text{ g cm}^{-3}$ ).
- Any prolonged thermal treatment, after the completed gypsum transformation into hemihydrate, is without a significant effect on the product quality and is cost-inefficient for future use in industrial processes.

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### VÝVOJ HYDROTHERMÁLNÍ TECHNIKY PŘÍPRAVY ALFA-HEMIHYDRÁTOVÉ SÁDRY ZE SÁDROVCE JAKO PRODUKTU ODSÍŘENÍ

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Sádrovec jako produkt odsíření spalovacích plynů při spalování fosilních paliv v průmyslových závodech byl upraven varem ve vodném roztoku chloridu sodného ( $C_{NaCl} = 3 \text{ mol l}^{-1}$ ) při koncentracích: 0,125, 0,250, 0,500, 0,750 a 1,000 gram sádrovce v ml roztoku. Výsledky ukázaly, že rychlost přeměny sádrovce roste s jeho koncentrací v roztoku. Produkt získaný při různých rychlostech přeměny obsahoval krystalickou fázi s odlišnou morfologií, velikostí a specifickým povrchem. Produkt s nejmenším specifickým povrchem byl získán při nejvyšší koncentraci sádrovce v roztoku. Dále bylo zjištěno, že prodloužení varu po vzniku hemihydrátu neovlivnilo významně kvalitu a tím cenovou náročnost budoucího průmyslového procesu.