

# THE TREATMENT OF GYPSUM AS A PRODUCT OF THE FLUE GAS DESULPHURIZATION PROCESS

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Submitted August 19, 2004; accepted November 28, 2004

**Keywords:** Alpha and beta hemihydrate, FGD gypsum, Hydrothermal method

*The modified hydrothermal method for the preparation of the alpha hemihydrate calcium sulphate was applied for the dehydration of gypsum as a product of the flue gas desulphurization process with the gypsum/acid solution mixing ratios 0.125, 0.250, 0.500 and 0.750 g/cm<sup>3</sup>. The obtained products were investigated by IR, DTA and microscopic analysis. The result of analysis indicated complete reaction at different rates, in the first three suspensions (0.125 - 0.500 g/cm<sup>3</sup>) giving a mixture of the both (alpha and beta) hemihydrate forms. In the suspension with the ratio 0.750 g/cm<sup>3</sup> the dehydration of gypsum was not complete. The results showed that an increasing the gypsum/acid solution mixing ratio brings an increase of the fraction of the superior alpha form in the final product, as well as an increase of the reaction rate and the average lengths of the alpha hemihydrate single crystals.*

## INTRODUCTION

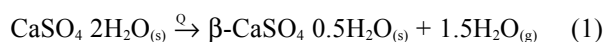
We live in a time of growing ecological problems. Modern industry gives us many attractive products which increase our living standard, but simultaneously it also results in many industrial wastes. The question is how to manage these wastes - to occupy agricultural land by their disposal and to pollute natural water and the atmosphere or to use them as raw materials for the manufacture of useful industrial products. Indeed there is no dilemma. The only real solution is the latter one - to use them as industrial raw materials.

Among fly ash and slag, the significant industrial waste, which is liberated in power plants in the large quantity, is waste gypsum. In these plants, gypsum is the product of the flue gas desulphurization process (FGD-gypsum). Gypsum is also a by-product of the production plants of some inorganic and organic acids, metals, pigments, nitrocellulose as well as the waste water (containing SO<sub>4</sub><sup>2-</sup> ions) purification etc. [1, 2, 3, 6].

All these waste gypsums are utilized worldwide as a surrogate for mineral gypsum for the manufacture of different products in the civil industry and also in medicine, dentistry, modelling etc.

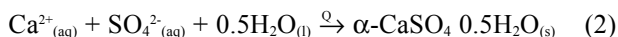
One of the most attractive products of the mineral gypsum is calcium sulphate hemihydrate (CaSO<sub>4</sub>·0.5H<sub>2</sub>O), which can be obtained by thermal treatment realized by "dry" or "wet" methods [5, 7, 8, 9, 10].

The "dry" method is based on the heating of gypsum at 130-150°C under atmospheric pressure. The product obtained by this method is an inferior form of hemihydrate, the so-called beta hemihydrate. In this method the liberated water vapour diffuses through the crystal layers significantly disturbing the structure of the crystal lattice, forming an incoherent granular structure with a rough surface and large surface area. This means that the following reaction occurs in the solid phase:



"Wet" methods is realized by heating the gypsum in an autoclave at temperatures between 110-160°C under elevated pressure in an atmosphere of saturated vapour (the autoclave method) or by boiling or near boiling solutions of an inorganic acids or their salts (which do not hydrolyze), under normal pressure (the hydrothermal method). The product of the hydrothermal methods is usually the superior alpha form of hemihydrate but also beta hemihydrate and anhydrite can be formed, depending of the process conditions [8]. This is the latest wet method developed and it is presented only in the literature. The fact that it is performed under atmospheric pressure and that the heat transfer from the liquid (solution) to solid (gypsum) phase is very efficient and uniform makes it very economic and promising. Also the possibility that impurities unusually present in waste gypsum can be dissolved in the appropriate by-selected solution make is suitable for this grade of gypsum [5, 14].

The mechanism of alpha hemihydrate formation by the hydrothermal method is not well investigated and there are many controversial statements in the literature. The dominant statement according to the published data is that a reaction occurs by dihydrate dissolution in the electrolytic solution which is followed by crystallization (the so called through-solution reaction mechanism) according to the following equation:



There are also statements that it occurs in the solid phase (according to reaction(1)), in which water molecules in the form of liquid drops slowly move through the layers, when slightly disturbing the crystal lattice structure [1, 2, 5]. In addition, the opinion of some authors is that both reaction mechanisms occur simultaneously [1, 2].

The different mechanisms of hemihydrate formation causes different degrees of perfection of their crystal lattice: in the alpha form it is higher than in the beta form. The different degree of perfection of the hemihydrate crystal lattice is manifested in their differential thermal analysis exotherms: for the alpha form, a large endotherm, which corresponds to the transformation of hemihydrate to soluble anhydrite, is directly followed by a small exotherm corresponding to the transformation of soluble to insoluble anhydrite. For the alpha form this exotherm is located at a lower temperature than that for the beta form, where it does not follow directly large endotherm. Hence DT analysis, together with microscopic analysis, can differentiate the hemihydrate forms. IR spectra and X-ray diffraction patterns of the two forms of this compounds are identical [3, 12, 14, 15].

The different mechanisms of hemihydrate formation also results in hemihydrate particles with different characteristics; the alpha form consists of transparent and translucent, compact, smooth, nonporous, regularly-shaped (needle, prism or rod like) single crystals and the beta form consists of white, soft and porous irregularly shaped particles. The different qualities of these forms results from the different surface areas of their particles and, consequently, of the different amounts of adsorbed water. Hence, the mechanical properties of the produced dihydrate are different. The smooth and compact particles of the alpha form require a smaller quantity of water to give the dihydrate which has better mechanical properties than the beta form [13].

In our previous works, the alpha form of the hemihydrate of calcium sulphate was obtained by a hydrothermal method, which consisted of stirring citro and nitrogypsum in unheated a 20 wt.% solution of sulphuric acid under atmospheric pressure [4, 17]. The aim of this work was to utilize this method with another type of waste gypsum, FGD-gypsum. The reason for the

selection of sulphuric acid solution as the liquid medium is also the possibility to obtain sulphuric acid in the unit for flue gas desulphurization.

## EXPERIMENTAL

The gypsum was analyzed by the classical chemical, IR (Perkin Elmer spectrophotometer Type 782) and microscopic (American Optical-Stereoscopic Microscope) analyses.

The experiments were performed in a discontinuous laboratory reactor with perfect mixing (600 revolutions per minute). The procedure was following: different masses of gypsum were immersed and mixed with constant volumes of an unheated 20 wt.% aqueous solution of sulphuric acid (gypsum/acid solution mixing ratios 0.125:0.25:0.50 and 0.75g/cm<sup>3</sup>) under atmospheric pressure for a given time interval.

Subsequently, the phases were separated by vacuum filtration and the product was rinsed with boiling water in order to remove the sulphate ions. After drying at 105°C, the samples were examined by qualitative IR, microscopic and DTA (Derivatograph C MOM, Budapest) analysis. The contact time of the phases, gypsum and acid solution, was successively prolonged by five minutes until hemihydrate formation was detected. In this way the time of dehydration was determined. In the experiments where hemihydrate was not formed, or was not formed completely, the contact time of the phases was prolonged to three hours.

## RESULTS AND DISCUSSION

The results of chemical analysis of the FGD gypsum are presented in table 1. Analysed CaO/SO<sub>3</sub> ratio being greater than the theoretical as well as the MgO content indicate the presence of carbonates as an impurities. This corresponds with the results of IR analysis (figure 1), showing carbonate band at 1450 cm<sup>-1</sup> [11].

The Enel specifications [16] for the reutilization of this sort of waste gypsum requires that the content of MgO and CaCO<sub>3</sub> can not exceed 0.01 and 1.5 wt.%, respectively. These impurities are the second reason for the utilization of sulphuric acid as the liquid medium. It was supposed that in this manner these misbalances can be corrected for the dissolution of the carbonate.

The microscopic analysis of the gypsum showed that it is consisted of microcrystals and their irregularly shaped aggregates, with a very narrow range of sizes and with the average particle diameter 0.074 mm, which implies that prior grinding and sieving is not a necessity.

The composition of the product and the time of gypsum dehydration, i.e. the time required for hemihy-

hydrate formation, were determined by periodical qualitative IR analysis, using the method presented in our previous paper [4]. The rate of gypsum dehydration rate was calculated by dividing the mass of dihydrate by the corresponding dehydration time. The obtained results are presented in table 2.

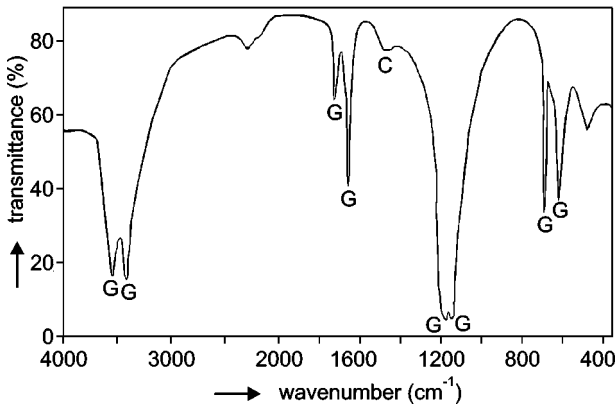


Figure 1. IR spectrum of FGD-gypsum.

Table 1. Chemical composition of the FGD gypsum.

Constituents	(wt.%)
SiO <sub>2</sub>	0.63
Al <sub>2</sub> O <sub>3</sub>	0.14
Fe <sub>2</sub> O <sub>3</sub>	0.38
CaO	32.80
MgO	2.18
SO <sub>3</sub>	45.72
P <sub>2</sub> O <sub>5</sub>	-
TiO <sub>2</sub>	-
Na <sub>2</sub> O	-
K <sub>2</sub> O	-
Loss on ignition	1.16
Crystal water	17.18
Σ	100.19
CaO/SO <sub>3</sub>	0.717

It can be seen, that the gypsum/acid solution ratio influences the product composition, characteristics and the gypsum dehydration rate. The hemihydrate of calcium sulphate was formed as the product in the experiments No.1-3. The highest gypsum/acid solution in the experiment No.4 brings not complete dehydration of gypsum, i.e. a mixture of hemihydrate and dihydrate was finally obtained. It is also evident that the increasing the gypsum/acid solution mixing ratio causes an increase in the rate of gypsum dehydration (No.1, 2 and 3).

The results of the microscopic examination of the hemihydrate showed, that in all experiments it consisted of two different morphological forms: the first composed of large, compact, smooth, needle like single crystals and the second consisted of porous, soft aggregates of microcrystals with diameters similar to those of the gypsum particles. According to literature data, the first form corresponds to the alpha and the second to the beta form of the hemihydrate of calcium sulphate. The amount of these forms depends of the gypsum/acid solution mixing ratio: the higher mixing ratio, the higher is the portion of the alpha form in the product, the large is the average length of the alpha hemihydrate single crystals and, according the literature data, the better are the utilization properties [1, 2]. These trends are also presented in table 2.

The results of the microscopic observations of the samples are in agreement with the result of DTA analysis (figures 2-4) showing the two small exothermic peaks. The first peak directly follows a large endotherm (characteristic for the alpha form) and the second peak at higher temperatures indicates the beta form of the hemihydrate. This means that dehydration reaction of gypsum occurs simultaneously - in the solution, giving the alpha form, and in the solid phase, giving the beta form of the hemihydrate (reactions (1) and (2)). Increasing the gypsum/acid solution mixing ratio causes an increase of the portion of the faster through-solution reaction giving the alpha form of the hemihydrate of calcium sulphate as the product. This is confirmed by the increase of temperatures of endothermic peaks (164, 166 and 169°C) at DTA curves (figures 2-4) indicating higher crystal lattice uniformity of obtained hemihydrate.

Table 2. The influence of the gypsum/acid solution mixing ratio on product composition, characteristics and the rate of its formation.

Exp.No	gypsum/acid solution mixing ratio (g/cm <sup>3</sup> )	composition of the product	α-form in the product (vol.%)	average length of particles (μm)		rate of gypsum dehydration (g/min)
				α-form	β-form	
1	0.125	H. H.*	9	8.5	0.072	0.29
2	0.250	H. H.	78	11.20	0.062	1.00
3	0.50	H. H.	88	15.00	0.058	2.50
4	0.75	D. H. + H. H.	-	-	-	-

\*H. H. - hemihydrate; D. H. - dihydrate

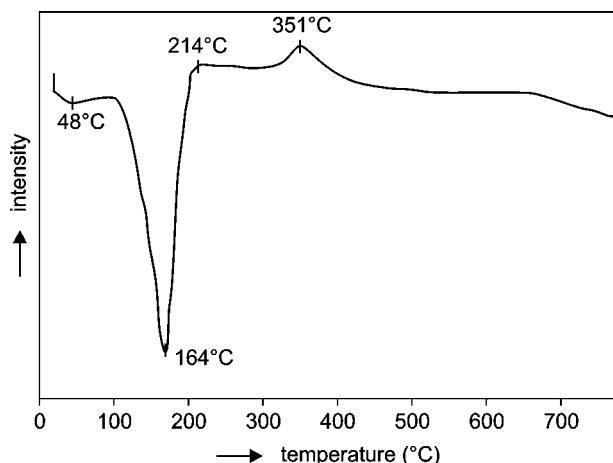


Figure 2. DTA curve for hemihydrate obtained for gypsum/acid solution mixing ratio 0.125 g/cm<sup>3</sup>.

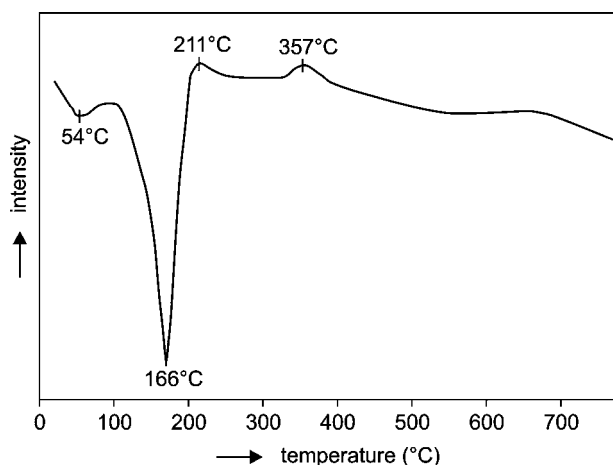


Figure 3. DTA curve for hemihydrate obtained for gypsum/acid solution mixing ratio 0.250 g/cm<sup>3</sup>.

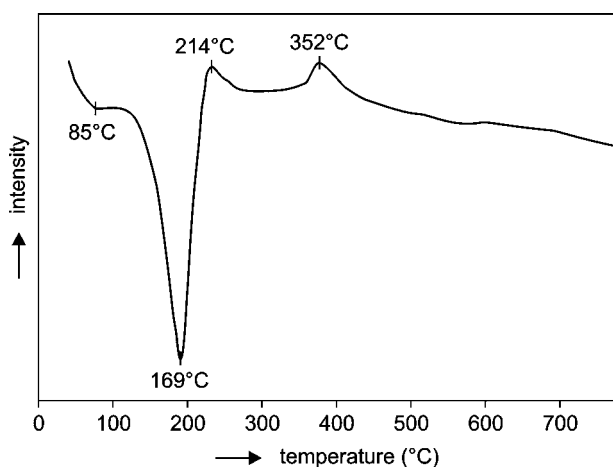


Figure 4. DTA curve for hemihydrate obtained for gypsum/acid solution mixing ratio 0.500 g/cm<sup>3</sup>.

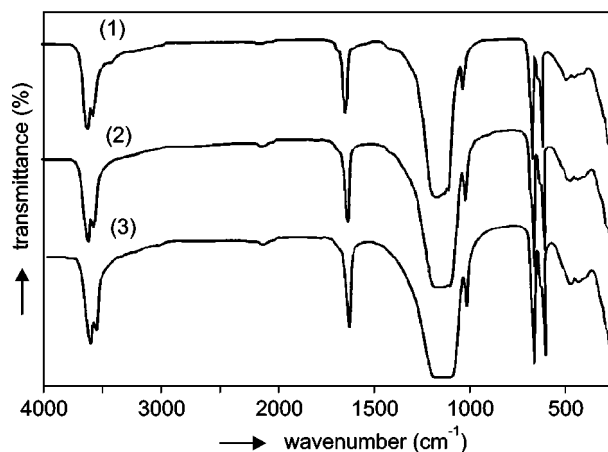


Figure 5. IR spectra of hemihydrates obtained for the gypsum/acid solution mixing ratios 0.125 (1), 0.250 (2) and 0.500 g/cm<sup>3</sup> (3).

Very small endothermal peaks at 48, 54 and 85°C on the DTA curves indicate low content of absorbed water in the products.

The IR spectra of the obtained hemihydrates confirmed the assumption that carbonates would be removed by dissolution in the acid solution (the absence of a band at 1450 cm<sup>-1</sup>, figure 3). Only the alpha form of the hemihydrate was obtained when citro and nitrogypsum were dehydrated by the same method [4, 17].

## CONCLUSIONS

On the basis of the obtained results, it can be concluded that:

- FGD gypsum dehydration and hemihydrate formation are possible by applying hydrothermal method, when preparing the gypsum suspension in unheated 20 wt.% aqueous solution of sulphuric acid under normal pressure at the gypsum/acid solution mixing ratios 0.125, 0.250 and 0.500 g/cm<sup>3</sup>.
- The obtained hemihydrate is carbonate free, even when primary FGD gypsum contained carbonates as impurities.
- Whereas dehydration of the citro and nitrogypsum using the same method brings pure alpha hemihydrate of calcium sulphate, in the case of FGD-gypsum a mixture of both alpha and beta form of the hemihydrate were obtained. The fraction of the superior alpha form, the rate of the gypsum dehydration reaction and the average lengths of single crystals of alpha hemihydrate increase with increasing gypsum/acid solution ratio from 0.250 to 0.500 g/cm<sup>3</sup>.
- For the gypsum/acid solution mixing ratio 0.750 g/cm<sup>3</sup>, the gypsum dehydration reaction is not complete, i.e. a mixture of hemihydrate and dihydrate was obtained.

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ÚPRAVA SÁDRY JAKO PRODUKTU ODSÍŘENÍ SPALIN

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Modifikovaná hydrotermální metoda přípravy alfa hemihydrátu síranu vápenatého byla použita pro hydrataci sádry jako produktu odsíření spalin při poměru sádra/roztok kyseliny 0,125, 0,250, 0,500 a 0,750 g/cm<sup>3</sup>. Získané produkty byly zkoumány IČ spektrometrií, DTA a mikroskopickou analýzou. Výsledky IČ spektrometrie ukázaly na kompletní průběh reakce probíhající různou rychlostí; v prvních třech suspenzích (0,125-0,500 g/cm<sup>3</sup>) vznikla směs alfa a beta hemihydrátu. Ve čtvrté suspenzi s poměrem 0,750 g/cm<sup>3</sup> neproběhla dehydratace kompletně. Výsledky ukázaly, že zvyšující se poměr sádra/roztok kyseliny přináší růst obsahu výsledné alfa formy hemihydrátu stejně jako růst rychlosti průběhu reakce a průměrné délky krystalů alfa hemihydrátu.