PRODUCTION OF CALCIUM SULPHATE ALPHA-HEMIHYDRATE FROM CITROGYPSUM IN UNHEATED SULPHURIC ACID SOLUTION

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Alpha-hemihydrate of calcium sulphate can be obtained by suspending gypsum in boiling or almost boiling aqueous solution of an inorganic acid salts or sulphuric acid at atmospheric pressure. Our task was to try to obtain it from citrogypsum in unheated solution of this acid. The experiment proved it possible if 10, 15, 20, 30, or 40 wt.% solution was used, and that the resulting alpha-hemihydrate developed at various ratios and had different properties, depending on the acid solution concentration and the gypsum/acid solution mixing ratio. An alpha-hemihydrate composed of smooth, compact, acicular monocrystals, which according to reference data promises the best utilitarian aspect, was obtained using 20 wt.% acid solution at 0.25 g cm^{-3} mixing ratio.

INTRODUCTION

Calcium–sulphate alpha–hemihydrate (α–CaSO$_4$·0.5 H$_2$O) can be produced by heating natural or synthetic calcium–sulphate dihydrate (CaSO$_4$·2 H$_2$O) in an autoclave to temperature over 100 °C (autoclave method). This method has been used only at the industrial level. The first industries for the autoclave production of alpha–hemihydrate by this method were built in Germany (Guilini) in 1962 and Japan (Nitto) in 1973 [1 – 4].

An alternative, the hydrothermal method, of alpha–hemihydrate production is proposed. It consists of dihydrate boiling, or nearly boiling, in aqueous solutions of concentrated salts (with or without surface–active substance) or inorganic acids, under atmospheric pressure. This is the latest developed method for alpha–hemihydrate production, described only in literature, which has not yet found the industrial application. The published information also states that the method is particularly suitable for waste gypsum beneficiations, because its impurities can dissolve and remain in the liquid phase [1, 5, 10, 11, 12]. The efficient and uniform heat transfer from liquid (solution) to solid (gypsum) phase and the operation under atmospheric pressure are the reasons why this method is employed to economically produce hemihydrate of good and uniform quality.

The mechanism of calcium sulphate alpha-hemihydrate formation from gypsum by this method has not yet been well studied and verified. Some information suggests that the reaction evolves in the solid phase. Water molecules slowly diffuse in drops from dihydrate interlayers (solids-state mechanism of the reaction). Others state that the reaction evolves in the solution, i.e. it is proceeded by dihydrate passing into the solution, where from alpha-hemihydrate separates by crystallization (through-solution mechanism of the reaction). There is also the opinion that the reaction simultaneously operates in both phases [2 - 5].

The alpha-hemihydrate grade rises with the compactness, smoothness and granulation of its crystals on which depends the water requirement controlling mechanical properties of the prepared dihydrate. A hemihydrate composed of smooth, compact, large monocrystals, as described in references, will give a dihydrate of good utilitarian properties.

In view of the fact that gypsum is a by–product in production processes of many organic and inorganic acids, nitrocellulose, pigments, metals and of gas desulphurisation processes (fossil fuel burning products in industrial plants - so called flue-gas gypsum) and that it is now, and most likely in the future as well, a significant ecological problem, the development and improvement of this method for industrial use has full economic justification [1, 9, 11-19].

In our experiment, an attempt is made to provoke the dehydration reaction of citrogypsum, a by–product of citric acid production, using unheated sulphuric acid solution in different concentrations (under atmospheric pressure), and thus obtain the alpha–hemihydrate product.

The reasons for selecting sulphuric acid solution as the liquid medium were the following: a) this acid can be simultaneously obtained in the flue gas desulphurization unit (on gas washing with water) with flue gas gypsum which is commonly obtained by gas washing with lime–water suspension; b) this acid is also a

Table 1. Classical chemical analysis of unwashed citro gypsum.

component	ignition loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
(wt.%)	2.7	0.83	0.15	0.24	39.28	0.50	55.88

by–product in the production of nitrocellulose (here waste gypsum is produced with acid neutralization by lime) and some other products, or is in common use in many processes giving waste gypsum.

It follows from the above stated that the development of the method, which includes the use of sulphuric acid solution in gypsum processing, has an economic justification because the cost of sulphuric acid does not (or in many circumstances does not significantly) incur a higher cost of the product.

Published information indicated that waste gypsum dehydration reaction occurs in 10, 15, 20, 40 wt.% solutions of sulphuric acid at temperatures higher than 90 °C (at atmospheric pressure) (1, 10). What happens at lower temperatures? Is it possible to develop the same reaction, without heating the liquid medium, within a reasonably long time for industrial usage? Answers to these questions were sought in the reported experimental study.

EXPERIMENTAL PART

Citrogypsum was subjected to the classical chemical, qualitative IR (Perkin Elmer 597), and micro-scopic (American Optical-Stereoscopic Microscope) analyses.

The experiment was performed in laboratory charge reactor with perfect mixing (n = 600 rpm) following the procedure: different quantities of citro-gypsum (2, 5, 10, 20, 30, 40 grams) were suspended in the equal volume (40 cm^3) of sulphuric acid solutions of different concentrations (2.5; 5; 10; 15; 20; 30; 40 wt.%) and stirred for a predetermined period.

The product was separated from the liquid phase by vacuum filtration, rinsed in water, dried at 105 °C, and examined in qualitative IR, microscopic and DT analyses (type AMINCO). The contact time of phases, solution and citrogypsum, was prolonged until the formation of hemihydrate. In cases of the hemihydrate non-formation or the product being a mixture of hemihydrate and dihydrate, the phase-contact time was prolonged to three hours.

RESULTS AND DISCUSSION

The results of classical chemical (table 1) and qualitative IR (figure 1) analyses indicate pure citro-gypsum substance which can be directly used in alpha-hemihydrate production without any pretreatment.

The microscopic analysis of citrogypsum showed its composition of thin-tabular, clear and transparent, colourless crystal aggregates without lustre (typo-morphic of gypsum) within a very narrow size range of
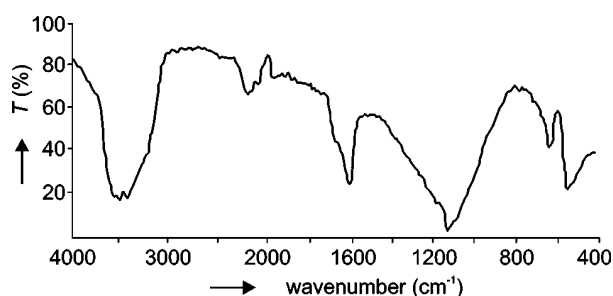
Figure 1. IR spectrum of citrogypsum.

0.2 mm average diameter. This implies its direct usability without any preliminary adjustment of size (grinding) or uniformity (sieving).

The composition of the product and the time of its formation were established in a periodical (5 min) qualitative IR analysis. The formation of hemihydrate was observed from the appearance of an IR spectral band at 3600 cm^{-1}, characteristic of hemihydrate, and
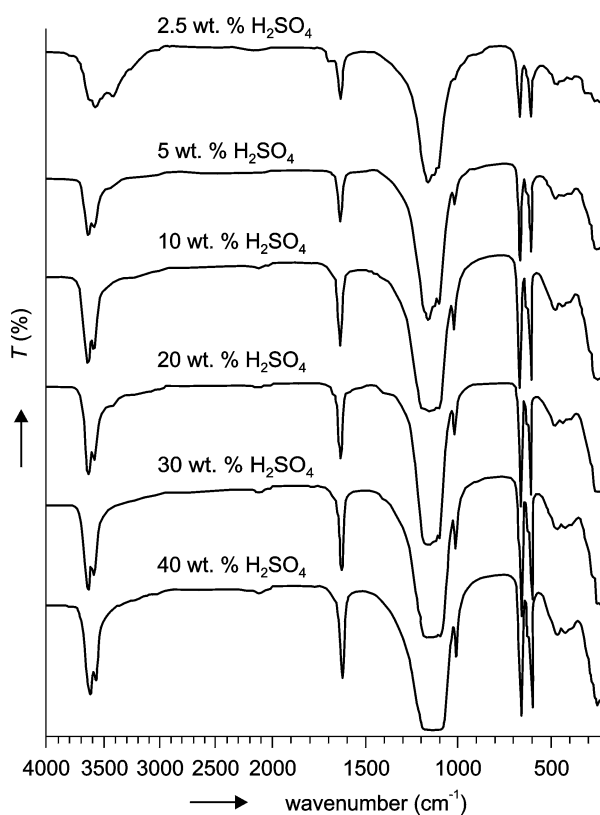
Figure 2. The influence of acid solution concentration on product composition (gypsum/acid solution mixing ratio 0.05 g cm^{-3}).

Table 2. The influence of acid concentration and gypsum/acid solution mixing ratio on product composition and time of hemihydrate formation.

No	acid concentration solution (wt.%)	gypsum/acid solution mixing ratio (g cm^{-3})	reaction product	time of hemihydrate formation (min)
1		0.050	DH+HH	
2		0.125	DH	
3	2.5	0.250	DH	
4		0.500	DH	
5		0.750	DH	
6		1.000	DH	
7		0.050	HH+DH	
8		0.125	DH+HH	
9	5.0	0.250	DH	
10		0.500	DH	
11		0.750	DH	
12		1.000	DH	
13		0.050	HH	40
14		0.125	HH+DH	
15	10.0	0.250	DH+HH	
16		0.500	DH	
17		0.750	DH	
18		1.000	DH	
19		0.050	HH	30
20		0.125	DH+HH	
21	15.0	0.250	DH	
22		0.500	DH	
23		0.750	DH	
24		1.000	DH	
25		0.050	HH	20
26		0.125	HH	16
27	20.0	0.250	HH	10
28		0.500	DH+HH	
29		0.750	DH+HH	
30		1.000	DH	
31		0.050	HH	15
32		0.125	HH+DH	
33	30.0	0.250	DH+HH	
34		0.500	DH	
35		0.750	DH	
36		1.000	DH	
37		0.050	HH	10
38		0.125	HH+DH	
39	40.0	0.250	HH+DH	
40		0.500	DH	
41		0.750	DH	
42		1.000	DH	

DH-dihydrate
HH-hemihydrate

the disappearance of the band at 1680 cm^{-1} typical of dihydrate figures 2 and 3 [6].

Alpha-modification of the hemihydrate was verified in microscopic and DT analyses [7].

The experimental results, presented in figures 2 and 3 and tables 2 and 3, show that acid solution concentration and gypsum/acid solution mixing ratio

have some effect on the product composition, time of hemihydrate formation, and its characteristics.

The calcium sulphate alpha-hemihydrate was formed when 10, 15, 20, 30, or 40 wt.% acid solution was used at the lowest gypsum/acid solution mixing ratio (experiments 13, 19, 25, 31, 37) and 20 wt.% H_2SO_4 at the mixing ratio values of 0.125 and
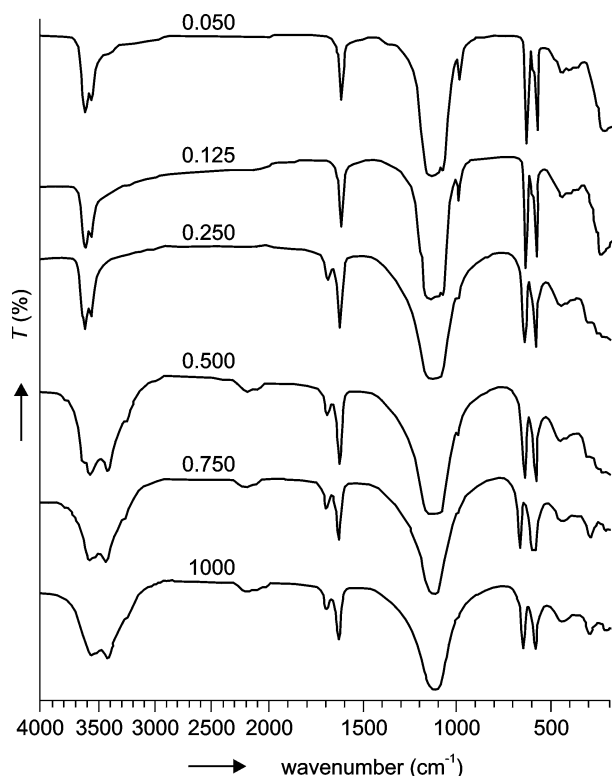
Figure 3. The influence of gypsum/acid solution mixing ratio on product composition (20 wt.% H_2SO_4).

0.250 g cm^{-3} (experiments 26, 27; table 2). In all other experiments, the obtained products were mixtures of dihydrate and hemihydrate, with the dihydrate rate rising with the increasing gypsum/acid solution mixing ratio or pure dihydrate.

The obtained alpha-hemihydrate is a mixture of two morphologically different phases: a phase of smooth, compact, clear, transparent, colourless, acicular monocrystals and a phase of typomorphic aggregates; with the increasing: a) acid concentration, the rate of monocrystal phase decreases and their lengths increase (experiments 1, 2, 3, 6, 7; table 3); b) gypsum/acid solution mixing ratio, the rate of monocrystals and their lengths increase and the time of their formation decrease (experiments 3, 4, 5; table 3 and experiments 25, 26, 27; table 2).

How to explain the results, primarily the fact that the alpha-hemihydrate was obtained in unheated solution of sulphuric acid? Its formation may probably be explained by the increased gypsum solubility in sulphuric acid, caused by the formation of a complex calcium compound [8].

CONCLUSIONS

The experimental results lead to the following statements:

Calcium sulphate alpha-hemihydrate was a product of citrogypsum suspension and stirring in aqueous solutions of sulphuric acid in concentrations of 10, 15, 20, 30, 40 wt.% at the gypsum/acid solution mixing ratio of 0.05 g cm^{-3} at room temperature. In acid solution of 20 wt.%, the hemihydrate was obtained also at the mixing ratio 0.125 or 0.250 g cm^{-3}.

The time of hemihydrate formation varied, decreasing with the increasing acid concentration and gypsum/acid solution ratio.

The obtained hemihydrate consisted of two morphologically different forms: one composed of compact, smooth, lustrous regular and clear acicular monocrystals, and second in tabular aggregates. With

Table 3. The influence of acid concentration and gypsum/acid solution mixing ratio on hemihydrate crystal morphology and dimensions.

acid concentration (wt.%)	gypsum/acid solution mixing ratio (g cm^{-3})	hemihydrate crystal morphology and dimensions
10	0.050	Sample made of two morphologically different phases: smooth compact colourless clear transparent acicular monocrystals (average length 16.2 μm), and typomorphic aggregates 50 μm in average diameter. Phase rate ≈50 wt.%.
15	0.050	Two phases as in exp. 1, only coarser aggregates (55 μm) and longer monocrystals (20 μm) and more abundant aggregates (≈60 wt.%).
20	0.050	Two phases as in exp. 1, only average crystal length 25 μm and aggregate diameter 60 μm. Aggregate rate ≈65 wt %.
20	0.125	Same as in exp. 1, only crystals more abundant (≈70 wt.%), average length 28 μm, and aggregates 70 μm average diameter.
20	0.250	Same as in exp. 1, only monocrystal rate ≈95 wt.% (average length 32 μm) and aggregates 82 μm average diameter.
30	0.050	Same as in exp. 1, only monocrystal rate ≈30 wt.% (average length 28 μm), and aggregates 62 μm in diameter.
40	0.050	Same as in exp. 1, only monocrystal rate ≈16 wt.% (average length 31 μm), and aggregates 65 μm average diameter.

the increasing acid concentration, the ratio of mono-crystals decreased and their lengths increased.

In acid solution of 20 wt.%, the ratio of mono-crystals and their lengths increased with the increasing gypsum/acid solution mixing ratio; for the ratio of 0.25 g cm^{-3}, the product had 95 wt.% of monocrystals, which, according to reference data, promises the best utilitarian value of dihydrate based on it.

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Submitted in English by the authors.

VÝROBA ALFA HEMIHYDRÁT SÍRANU VÁPENATÉHO
Z ODPADNÍHO SÁDROVCE
V ROZTOKU KYSELINY SÍROVÉ

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Alfa hemihydrát síranu vápenatého může být získán suspenzováním sádrovce do roztoku solí anorganických kyselin nebo kyseliny sírové při atmosférickém tlaku a teplotě varu nebo blízké varu roztoku. Naším cílem bylo pokusit se získat hemihydrát z odpadního sádrovce při výrobě kyseliny citrónové. Experiementy potvrdily tuto možnost pokud se použije 10, 15, 20, 30 nebo 40% roztok. Výsledný produkt měl odlišné vlastnosti v závislosti na koncentraci kyseliny a poměru míchání sádrovec - roztok kyseliny. Alfa-hemihydrát složený z hladkých kompaktních jehlicovitých krystalů, které podle referenčních dat slibují nejlepší užitkovou hodnotu byla získána použitím 20 hmotn.% roztoku kyseliny sírové při poměru míchání 0,25 g sádrovce na 1 ml roztoku.