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HYDROTHERMAL TREATMENT TIME EFFECT ON THE QUALITY OF ALPHA-HEMIHYDRATE FROM SELENITE

Hydrothermal treatment of selenite in concentrated either $CaCl_2$ or LiCl solutions requires a longer time than is necessary for complete inversion of selenite. For processes which occur in the solution (crystal formation from the solution and crystal growth in the solution), a longer hydrothermal treatment allows production of alpha-hemihydrate of a better quality (smaller specific surface area). It is possible to establish the optimum time of hydrothermal treatment-minimum time for the formation of the best quality product (smallest specific surface area).

1. INTRODUCTION

Thermal treatments of calcium-sulphate dihydrate by "dry method" and the inferior quality of its hemihydrate product, i.e. beta-form, and by "wet method" giving a superior alpha-form, have been known in literature (Fraunhofer, 1975; Butt, 1965; Singh, 1988; Fowler, 1968).

The "wet" techniques for production of alpha-hemihydrate include the hydrothermal treatment which consists of calcium-sulphate dihydrate boiling in concentrated salt or acid solutions at atmospheric pressure.

The "dry" thermal treatment of calcium-sulphate dihydrate is a simple technique, because it involves a single reaction in solid phase - inversion of dihydrate into hemihydrate.

Unlike the above, hydrothermal treatment is quite complex as it involves more than one process: dissolution of solid $CaSO_4 \cdot 2H_2O$ under the effect of electrolyte ions in the solution; $CaSO_4 \cdot 2H_2O$ dehydration reaction and formation of $CaSO_4 \cdot 1/2H_2O$ in solid phase; formation of α-$CaSO_4 \cdot 1/2H_2O$ crystals from the solution and α-$CaSO_4 \cdot 1/2H_2O$ crystal growth in the solution.

The time of "dry" treatment is easy to define. The process not longer than the time necessary for inversion of all of the dihydrate into hemihydrate is economical, because a prolonged treatment has no effect on the product quality.

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The question, what time should be allowed for a hydrothermal treatment, is a complex one. The time until the complete dihydrate inversion (its absence in solid phase) seems economical, but will it permit the formation of the best-quality α-hemihydrate, knowing that the reaction in solid phase is parallelled with processes in the solution (first of all the crystal growth)?

Our task was to study the problem and establish the optimum time of the hydrothermal treatment, i.e. the shortest time for production of the best α-hemihydrate (of smallest specific area). For this purpose we treated hydrothermally selenite in either $CaCl_2$ or LiCl solutions of 5M concentration until the complete selenite inversion (dihydrate disappearance from solid phase) and for different extended periods (5, 10, 20, 30, minutes). The time of complete selenite inversion (when the solid phase is without calcium-sulphate dihydrate) was determined using qualitative IR analysis. The products were analysed by qualitative IR analysis, DTA and X-ray analysis. Physical properties of the product were determined using microscopy (for crystal forms) and BET method (for specific surface areas).

2. EXPERIMENTAL

Natural selenite mineral of high purity (0.11% impurity) was used in the experiment. The procedure was the following:

1. Ten grams of selenite, size class 0.25-0.5 mm, was boiled in 30 cm^3 5M $CaCl_2$ (or LiCl) solutions (at atmospheric pressure) for different periods of time, successively extended by one minute (1 min., 2 min., 3 min., etc.).

2. IR spectra were recorded for solid samples (obtained as described in paragraph 1) and compared with IR spectra for $CaSO_4 \cdot 2H_2O$ and $CaSO_4 \cdot 1/2H_2O$ taken from reference literature (Nyguist, 1971; Gadsden, 1975; Bensted, 1968). This served to determine the time when solid samples had no more dihydrate but only hemihydrate, i.e. the time of complete selenite inversion.

3. Ten grams of selenite, size class 0.25-0.5 mm, was boiled in 30 cm^3 5M $CaCl_2$ or LiCl solutions in intervals 5, 10, 20, 30 minutes longer than that of complete selenite inversion (determined in paragraph 2).

4. The products obtained in 5M $CaCl_2$ and LiCl solutions within the time of complete selenite inversion, and products obtained as described in paragraph 3, were analysed by IR, DTA, and X-ray methods.

5. Physical properties of all the mentioned products were analysed under microscope (for crystal forms) and using BET method (for specific surface areas). The experiments were performed in a reactor with a constant rate of the magnetic stirrer (300 rpm). In each experiment, solid product was washed with boiling distilled water (until the reaction on Cl^- ions became negative) and dried in a dryer at 105°C before being analysed by the mentioned instrumental methods. Infrared absorption spectra were recorded by Perkin-Elmer spectrophotometer (type 397) in the range from 4000 to 400 cm^{-1}, using KBr pressed disc technique. For the X-ray analysis, Philips PW 1710 diffractometer was used. The angular range was 0-60° (2θ), because the peaks of the highest intensities on diffractogram occurred within this range for calcium-sulphate hemihydrate; d-values, angle and peak intensity values were computer registered. The Chevenard Joimer instrument of type A.D.A.M.E.L. was used to obtain differential thermal analysis curves in the temperature range from room temperature to 350 °C. Microscopical observations were carried out with an American Optical Stereoscopic ZOOM microscope. Specific surface area was determined by BET method using a Flowsorb II 2300 (Micrometrics) instrument.

3. RESULTS AND DISCUSSION

The infrared spectra which were used in determining the time of complete selenite transformation are shown in the Figure 1. These are IR spectra of the products obtained by heating 10 g of selenite (0.25-0.5 mm) in 30 cm^3 5M $CaCl_2$ solution for 1, 2, 3, 4, and 5 minutes.

Typical peaks, labelled B for selenite and A for hemihydrate, in these spectra show the presence of selenite or hemihydrate in the products. The figure shows a low inversion of selenite into hemihydrate after one-minute heating. With an extension of time, the intensity of peaks due to the presence of hemihydrate (A) increases, and that of selenite (B) decreases. Complete inversion of selenite is achieved in five minutes. The time of complete selenite inversion in 5M LiCl solution was determined in the same way, and was four minutes.

Qualitative IR-analysis of all products (obtained for time intervals of 5, 10, 15, 25, and 35 minutes in $CaCl_2$ solution and for 4, 9, 14, 24, and 34 minutes in LiCl solution) indicated the same substance in chemical composition, $CaSO_4 \cdot 1/2H_2O$. IR-spectra of all these products had identical bands at about: 3615 cm^{-1}, 3560 cm^{-1}, 1630 cm^{-1}, 1160-1090 cm^{-1}, 660 cm^{-1}, and 600 cm^{-1}, which according to

reference data (Nyquinst, 1971; Gadsden, 1975; Bensted, 1968) corresponded to calcium-sulphate hemihydrate. X-ray diffraction data for products are given in Table 1.

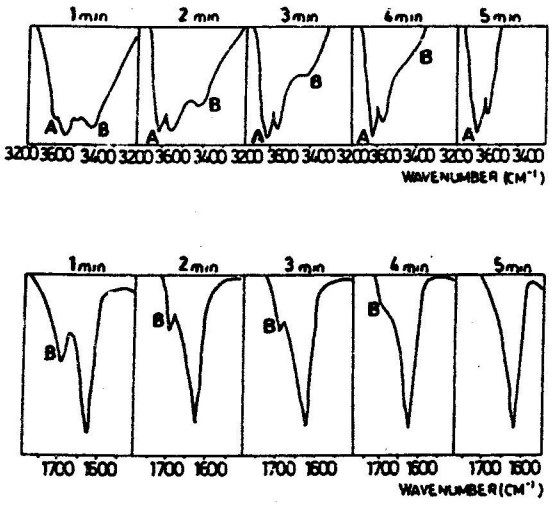

Fig. 1. IR spectra of samples prepared from selenite (0.25-0.5 mm) in 5M $CaCl_2$ solution, B: 3410 cm^{-1} and 1680 cm^{-1}; A: 3615 cm^{-1}

For all ten products, as indicated by data in Table 1, peaks occur for d-values which approximate d-values given in literature (Combe, 1968) for $CaSO_4 \cdot 1/2H_2O$. Consequently, X-ray diffraction data verified the same substance of all ten products: calcium-sulfate hemihydrate.

Table 1. X-ray diffraction data for products

$CaSO_4 \cdot 1/2\ H_2O$ (8)			Product 1		Product 2	
α(A°)	I/I_o(%)	hkl	α(A°)	I/I_o(%)	α(A°)	I/I_o(%)
6.0	70	101	5.9528	75.96	5.9788	80.33
3.469	55	301.002	3.4524	44.56	3.4616	42.11
3.006	100	400.202	2.9923	100.00	2.9967	100.00
			2.8010	6.86		
2.807	85	240.141	2.7938	6.09	2.8036	7.5
2.139	20	521.422	2.1332	6.22	2.1361	6.52
			1.8473	6.34		
1.847	55	442.143	1.8439	9.14	1.8462	9.85
1.6674	9	701.503	1.6639	6.47	1.6635	6.38

Table 1. (Continued)

Product 3		Product 4		Product 5		Product 6	
$\alpha(A_o)$	$I/I_o(\%)$	$\alpha(A_o)$	$I/I_o(\%)$	$\alpha(A_o)$	$I/I_o(\%)$	$\alpha(A_o)$	$I/I_o(\%)$
5.9748	75.63	5.9808	60.36	5.9588	78.29	5.9848	77.02
						3.4689	36.19
3.4576	45.28	3.4609	43.76	3.4517	41.47	3.4603	45.49
2.9977	100.00					3.0011	100.00
2.9879	45.63	2.9987	100.00	2.9926	100.00	2.9952	85.95
2.8019	6.52	2.8014	4.42	2.7963	8.44	2.8023	5.49
2.1361	7.5	2.1359	6.98	2.1325	7.27	2.1356	7.76
1.8459	9.03	1.8467	8.85	1.8445	10.03	1.8467	8.81
1.6649	7.22	1.6639	6.84	1.6632	6.85	1.6650	6.92

Product 7		Product 8		Product 9		Product 10	
$\alpha(A°)$	$I/I_o(\%)$	$\alpha(A°)$	$I/I_o(\%)$	$\alpha(A°)$	$I/I_o(\%)$	$\alpha(A°)$	$I/I_o(\%)$
5.9934	79.17	5.9488	69.25	5.9794	89.09	5.9874	87.49
3.4696	42.97			3.4669	37.36		
3.4623	42.45	3.4517	42.34	3.4583	40.21	3.4649	37.70
3.0039	100.00	2.9923	100.00	3.0044	96.70		
2.9951	66.10	2.9855	67.84	2.9966	100.00	3.0015	100.00
2.8057	8.15	2.7942	3.48	2.8074	12.34	2.8062	10.56
2.1373	8.49	2.1323	5.91	2.1353	8.23	2.1361	6.59
1.8475	10.55			1.8475	13.39		
1.8422	4.44	1.8426	5.26	1.8417	6.02	1.8492	10.21
1.6664	7.27	1.6639	7.69	1.6657	6.33	1.6662	5.79

*Products 1, 2, 3, 4 and 5 are obtained for 5M $CaCl_2$ in time intervals: 5, 10, 15, 25 and 35 minutes. Products 6, 7, 8, 9 and 10 are obtained for 5M LiCl in time intervals: 4, 9, 14, 24 and 34 minutes.

Table 2 shows endothermal and exotermal peaks from the differential thermal analysis curves of products. DATA results indicate

*Table 2. Differential thermal analysis data**

	Endothermal peak (°C)	Exothermal peak (°C)
Product 1	197	216
Product 2	197	217
Product 3	198	216
Product 4	202	219
Product 5	202	217
Product 6	198	217
Product 7	197	218
Product 8	199	219
Product 9	203	221
Product 10	201	220

*Product numbers are the same as in Table 1.

the endothermal and exothermal peaks of all differential thermal analysis curves approximately at 200°C and 220°C, respectively. According to reference data (Butt, 1965; Combe, 1968), these peaks are contained in the differential thermal analysis curve for α-hemihydrate, which means that all obtained products were α-$CaSO_4 \cdot 1/2H_2O$ (β-form has endothermal peak at 170-180°C and exothermal one at 320-360°C).

Physical properties (crystal form and specific surface area) of products are given in Table 3. The inferences based on data given in Table 3 are the following:

1. When the hydrothermal treatment for production of α-hemihydrate is the shortest, i.e. within the time required for complete inversion of selenite (experiments 1 and 6), the products include microcrystals and monocrystals, and are of the worst quality, or have large specific surface areas.

Table 3. Crystal forms and specific surface areas of products

No	Product obtained	Crystal form	Specific surface area (m^2/g)
1.	in 5M $CaCl_2$ for 5 min (time of complete selenite inversion)	Microcrystal aggregates and small amount of needle-like monocrystals	1.2
2.	in 5M $CaCl_2$ for 10 min	microcrystal aggregates and needle-like monocrystals	0.7
3.	in 5M $CaCl_2$ for 15 min	needle-like monocrystals	0.6
4.	in 5M $CaCl_2$ for 25 min	needle-like monocrystals	0.6
5.	in 5M $CaCl_2$ for 35 min	needle-like monocrystals	0.6
6.	in 5M LiCl for 4 min (time of complete selenite inversion)	microcrystal aggregates and needle-like monocrystals	0.8
7.	in 5M LiCl for 9 min	small amount of micro-crystal aggregates and needle-like monocrystals	0.4
8.	in 5M LiCl for 14 min	needle-like monocrystals	0.3
9.	in 5M LiCl for 24 min	needle-like monocrystals	0.3
10	in 5M LiCl for 34 min	needle-like monocrystals	0.3

2. At an extended time of hydrothermal treatment (experiments 2-5 and 7-10), conditions are provided for microcrystal growth in the solution, with the result of a reduced amount of microcrystals, increased monocrystals, until only monocrystals are contained. The

decrease in microcrystals and increase in monocrystals are accompanied by a reduction in their specific surface areas.

3. After some time of hydrothermal treatment (10 min. longer than that necessary for complete selenite inversion, experiments 3 and 8), the highest reduction of specific surface area is attained (2 times in 5M $CaCl_2$; and 2.7 times in 5M LiCl); further extension of time has no effect on the specific surface area reduction (experiments 4, 5, 9 and 10). This time is the optimum time of hydrothermal treatment for α-hemihydrate production from selenite.

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Hydrotermalna obróbka selenitu w stężonych roztworach $CaCl_2$ i LiCl dla otrzymania α-półhydratu wymaga dłuższego czasu niż w procesie całkowitej przemiany selenitu. Dłuższy czas obróbki hydrotermalnej pozwala na powstawanie α-półhydratu o lepszej jakości, gdyż tworzą się kryształy o mniejszym rozwinięciu powierzchni. Możliwe jest ustalenie optymalnego czasu obróbki hydrotermalnej, odpowiadającego minimalnemu czasowi tworzenia produktu o niewielkim rozwinięciu powierzchni.