PRODUCTS OF HYDROTHERMAL TREATMENT OF SELENITE IN POTASSIUM CHLORIDE SOLUTIONS

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Abstract

Selenite was boiled in KCl solutions of different concentrations at the respective boiling temperatures and atmospheric pressure. The products were subjected to X-ray diffraction analysis, qualitative infrared analysis, differential thermal analysis and microscopic examination. The product obtained in 1.0 M KCl solution was the β-form of calcium sulphate hemihydrate (β-$CaSO_4 \cdot 0.5H_2O$). In more concentrated KCl solution (1.5, 2.0, 2.5, 3.0, 3.5 or 4.0 M), the α-form of calcium sulphate hemihydrate (α-$CaSO_4 \cdot 0.5H_2O$) was formed, and a reaction took place between KCl and $CaSO_4$, which gave a double salt: potassium pentacalcium sulphate monohydrate ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$).

Keywords: calcium sulphate hemihydrate, differential thermal analysis, hydrothermal treatment, infrared analysis, selenite, X-ray diffraction

Introduction

Hydrothermal treatment of gypsum in a liquid medium, either in water at an increased pressure at a temperature between 110 and 160°C [1] or in aqueous solutions of salts and inorganic acids at the respective boiling temperatures and atmospheric pressure [2–4], involves a process which has not been widely studied.

The solubility of gypsum ($CaSO_4 \cdot 2H_2O$) in water is low, but it increases in the presence of electrolytes, such as inorganic acids and salts [5–8]. In aqueous medium, at temperatures exceeding 97°C [9, 10], calcium sulphate hemihydrate ($CaSO_4 \cdot 0.5H_2O$) is less soluble than calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$). These two facts account for the crystallization of $CaSO_4 \cdot 0.5H_2O$ from solution when $CaSO_4 \cdot 2H_2O$ is boiled in an aqueous solution of the salt and inorganic acid. The reaction can be described as

$$Ca^{2+}_{(aq)} + SO_4^{2-}_{(aq)} + 0.5H_2O_{(l)} = CaSO_4 \cdot 0.5H_2O_{(s)}$$
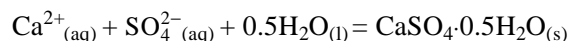
The resulting crystals may be regular (needles or prisms) and quite compact, when they are referred to as the α-form of the hemihydrate [2].

When conditions are not provided for crystallization of the hemihydrate from the solution, dehydration of the solid dihydrate produces the β-form of the hemihydrate, which consists of porous and irregular aggregates of microcrystals [2].

Hydrothermal treatment of the dihydrate in salt solutions enhances the production of high-grade hemihydrate, the process being complex and with limitations. The number of salts that can be used in aqueous solutions as liquid media for the treatment is not high; the salts must be well soluble in water without being hydrolysed, and must give colourless aqueous solutions. Salts of alkali metals (Li, Na, K, Rb and Cs) and alkaline earth metals (Ca, Sr and Ba) meet the conditions, but their use may be limited in view of the possible interactions of the salts and $CaSO_4$. Such reactions between the salts and $CaSO_4$ may produce undesirable compounds and/or the salt ions may penetrate the hemihydrate crystal lattice as it crystallizes from the solution.

The hydrothermal treatment of selenite in NaCl, LiCl or $CaCl_2$ solution was tested and reported earlier [11, 12]. It was found that NaCl in solution could react with $CaSO_4$, whereas a similar reaction did not occur in LiCl or $CaCl_2$ solution. For further development of the method of calcium sulphate dihydrate hydrothermal treatment, we boiled selenite in KCl solutions of different concentrations (1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 M)and studied the products by means of X-ray diffraction analysis (XRD), infrared (IR), spectroscopic analysis, differential thermal analysis (DTA) and microscopy.

Experimental

Natural selenite mineral of very high chemical purity (0.33 mass% impurity) was used in the experiment. Its chemical composition, determined by conventional chemical analysis, is given in Table 1.

Ten grams of selenite, size fraction –0.250+0.125 mm, was boiled in 50 cm^3 of aqueous KCl solution of different concentrations (1.0, 1.5, 2.0, 2.5, 3.0, 3.5 or 4.0 M) at the respective boiling temperature and atmospheric pressure. The boiling vessel was a reactor equipped with a magnetic stirrer (200 rpm). The solution concentration was maintained constant by continuously feeding in boiling distilled water to balance the water loss due to evaporation.

The periods during which the selenite was boiled with the different concentrations of KCl solution were as follows: 300 min for 1.0 M, 240 min for 1.5 M, 180 min for 2.0 M, 150 min for 2.5 M, 120 min for 3.0 M, 90 min for 3.5 M, and 75 min for 4.0 M, as determined in preliminary experiments. In a qualitative IR

Table 1 Chemical composition of selenite (mass%)

H_2O	20.75
CaO	32.47
SO_3	46.45
SiO_2 (insol.)	0.03
MgO	0.08

analysis, the intensities of the absorption bands characteristic of $CaSO_4 \cdot 2H_2O$ [13] at 3410 and 1688 cm^{-1} decreased as a function of time. The disappearance of these bands was used to determine the period necessary for transformation of all of the selenite into the product, or the duration of boiling the selenite in the various solutions of fixed KCl concentration.

The solid products of selenite after boiling for the determined time intervals were separated from the solution by vacuum filtration, rinsed in boiled distilled water to remove any trace of Cl^-, and dried at 105^oC for XRD, IR spectroscopic, DTA and microscopic examination.

The chemical compositions of the products were determined by the XRD powder technique. All samples were examined under the same conditions, using a Philips PW 1729 X-ray generator, a Philips PW 1710 diffractometer and the original APD software. The radiation source was an X-ray LLF tube with copper radiation and a graphite monochromator. The radiation was $\lambda CuK_{\alpha 1}=0.15405$ nm. The anode tube load was 40 kV and 35 mA. Slits of 1.0 and 0.1 mm were fixed. Samples were pressed into standard aluminium frames and measured in the 2θ range from 5° to 100°. Each $1/50^o$ (0.02^o) was measured for 0.5 s. For product identification, the MPDS program and JCPDS (ASTM) card files were used.

IR absorption spectra were recorded with a Perkin Elmer spectrophotometer 782 in the range from 4000 to 400 cm^{-1}, using the KBr pressed disc technique.

A Derivatograph C (MOM, Budapest) was used for the DTA. Platinum sample holders were used. The sample mass was 0.040 g, and the atmosphere was air. A Pt/Pt–Rh thermocouple was used, and the furnace heating was linear. The heating rate was 20^oC min^{-1}, in the range from 20 to 1050^oC; the recording period was 53 min. For data processing, the derivatograph data handling program V 2.1 was used.

Microscopic examinations were carried out with an American Optical Stereoscopic ZOOM microscope.

Results and discussion

The X-ray analytical results on the given products can be interpreted by using JCPDS (ASTM) cards 33-310 for $CaSO_4 \cdot 0.5H_2O$ (bassanite) and 18-997 for $K_2Ca_5(SO_4)_6 \cdot H_2O$ (görgeyite).

Table 2 shows the interplanar spacings (d), reflection intensities (I), and $h\,k\,l$ values taken from the two cards for the mentioned substances, and the interplanar spacings (d) and reflection intensities (I) for each of the products.

The data in Table 2 indicate that the product obtained when selenite is boiled in 1.0 M KCl solution is $CaSO_4 \cdot 0.5H_2O$, and that all other products (in 1.5–4.0 M KCl solution) are mixtures of $CaSO_4 \cdot 0.5H_2O$ and $K_2Ca_5(SO_4)_6 \cdot H_2O$.

The IR absorption spectra of the products obtained in 1.0 M and 2.0 M KCl solution are shown in Fig. 1. The IR spectra of all the other products (in 1.5, 2.5, 3.0, 3.5 and 4.0 M KCl solutions) are almost identical with that of the product in 2.0 M KCl solution, which is congruous with the X-ray data, and confirms the identity in chemical composition of the products and the difference of the product obtained in 1.0 M KCl solution.

Table 2a X-ray diffraction data on $CaSO_4 \cdot 0.5H_2O$, $K_2Ca_5(SO_4)_6 \cdot H_2O$ and the products from 1.0–1.5 M KCl

$CaSO_4 \cdot 0.5H_2O$*			$K_2Ca_5(SO_4)_6 \cdot H_2O$**			1.0M KCl		1.5M KCl	
d/nm	h k l	I/%	d/nm	h k l	I/%	d/nm	I/%	d/nm	I/%
0.6000	1 0 1	70	0.6270	1 1 0	8	–	–	0.6274	8
			0.5600	1 1 1	14	0.5984	55	0.5991	11
						–	–	0.5598	13
0.3469	3 0 1, 0 0 2	55	0.3420	0 2 0	10	0.3462	53	0.3463	7
			0.3370	3 1 2	8	–	–	0.3415	6
						–	–	0.3367	11
			0.3160	4 0 2	70	–	–	0.3162	21
0.3006	4 0 0, 2 0 2	100	0.3010	2 2 1	100	0.3002	100	0.3006	100
0.2807	2 4 0, 1 4 1	85				0.2806	56	–	–
			0.2756	3 1 6	30	–	–	0.2757	3
0.2139	5 2 1, 4 2 2	20				0.2138	19	0.2134	7
0.1847	4 4 2, 1 4 3	55				0.1847	34	0.1843	7
			0.1796	6 2 3	10	–	–	0.1796	4
0.1667	7 0 1, 5 0 3	9				0.1665	10	0.1666	2

* Nat. Bur. Stand. (U. S.) Monogr., 25, 18 22 (1981)
** Braitsch. N. Jb. Min. Mh., 126 (1965)

Table 2b X-ray diffraction data on the products from 2.0–4.0 M KCl

2.0M KCl		2.5M KCl		3.0M KCl		3.5M KCl		4.0M KCl	
d/nm	I/%	d/nm	I/%	d/nm	I/%	d/nm	I/%	d/nm	I/%
0.6283	7	0.6294	8	0.6273	7	0.6294	8	0.6274	7
0.5995	14	0.6008	16	0.5988	24	0.5999	18	0.5999	16
0.5599	13	0.5610	11	0.5597	12	0.5609	12	0.5598	12
0.3464	11	0.3469	12	0.3460	17	0.3468	13	0.3469	12
0.3416	6	0.3421	6	0.3415	5	0.3421	5	0.3421	6
0.3367	11	0.3371	13	0.3364	12	0.3370	15	0.3371	15
0.3164	23	0.3167	35	0.3162	30	0.3167	33	0.3167	33
0.3006	100	0.3010	100	0.3005	100	0.3009	100	0.3010	100
0.2812	8	0.2813	13	0.2808	9	–	–	–	–
0.2757	5	0.2761	8	0.2755	4	0.2762	4	0.2757	5
0.2135	6	0.2136	9	0.2137	6	0.2137	7	0.2137	6
0.1844	7	0.1845	14	0.1847	8	0.1845	10	0.1845	10
0.1797	4	0.1797	7	0.1795	5	0.1798	6	0.1797	7
0.1666	2	0.1668	2	0.1666	3	0.1667	3	0.1666	3

The IR spectrum of the product obtained in 1.0 M KCl solution (Fig. 1, a) contains only absorption bands which are characteristic [13–16] of $CaSO_4 \cdot 0.5H_2O$, at 3610 cm^{-1} (ν_3, H_2O), 3560 cm^{-1} (ν_1, H_2O), 1620 cm^{-1} (ν_2, H_2O), 1155, 1115 and 1095 cm^{-1} (ν_3, SO_4^{2-}), 1008 cm^{-1} (ν_1, SO_4^{2-}), 660, 630 and 600 cm^{-1} (ν_4, SO_4^{2-}).

Besides the mentioned absorption bands characteristic of $CaSO_4 \cdot 0.5H_2O$, the IR spectra of the product in 2.0 M KCl solution (Fig. 1, b) and of the products obtained in 1.5, 2.5, 3.0, 3.5 and 4.0 M KCl solutions contain absorption bands at 3530, 1180, 1075, 1000, 650 and 615 cm^{-1}. These bands confirm the presence of $K_2Ca_5(SO_4)_6 \cdot H_2O$, in addition to $CaSO_4 \cdot 0.5H_2O$, in the products as detected on XRD analysis. The absorption band at 3530 cm^{-1} originates from the stretching vibration of water (ν_1), those at 1180, 1075 and 1000 cm^{-1} from the stretching vibration of SO_4^{2-} (ν_3, ν_1), and those at 650 and 615 cm^{-1} from the bending vibration of SO_4^{2-} (ν_4) in $K_2Ca_5(SO_4)_6 \cdot H_2O$ [15].

DTA data on the products are presented in Table 3 and Fig. 2.
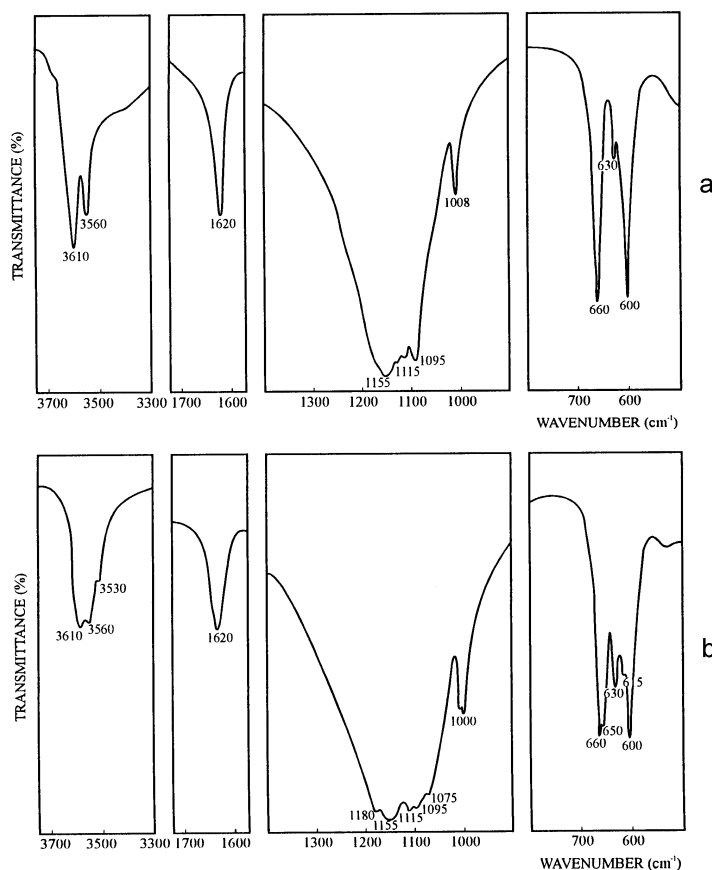

Fig. 1 IR-absorption spectra of products: a − in 1.0 M KCl solution, b − in 2.0 M KCl solution

As indicated by the presented data (Table 3 and Fig. 2), the differential curve of the product obtained in 1.0 M KCl solution exhibits an endothermal and an exothermal peak, whereas those of all other products display three endothermal peaks. The endothermal peak at 170^oC and the exothermal peak at 360^oC are peaks of β-$CaSO_4 \cdot 0.5H_2O$ [3, 10 17], which means that the product obtained in 1.0 M KCl solution was the β-form of the hemihydrate (Table 3 and Fig. 2). The first endothermal peaks in the differential curves of the other products (Table 3 and Fig. 2) corroborate the presence of α-$CaSO_4 \cdot 0.5H_2O$, and the second and third peaks the presence of $K_2Ca_5(SO_4)_6 \cdot H_2O$. The first endothermal peaks (at 128, 130, 129, 146 and 145^oC) correspond to α-$CaSO_4 \cdot 0.5H_2O$ dehydration and are not accompanied by exothermal peaks [3, 4, 18] as in the case of β-$CaSO_4 \cdot 0.5H_2O$. These peaks appear at lower temperatures than those in the literature, which implies a lower crystallinity of the obtained α-hemihydrate. Other endothermal peaks, at 478, 478, 475, 480, 460 and 460^oC (Table 3 and Fig. 2), correspond to the dehydration of $K_2Ca_5(SO_4)_6 \cdot H_2O$, and the third endothermal peaks, at 930, 930, 920, 930, 920 and 920^oC (Table 3 and Fig. 2), to the decomposition of the double salt [19, 20].

Table 3 DTA data

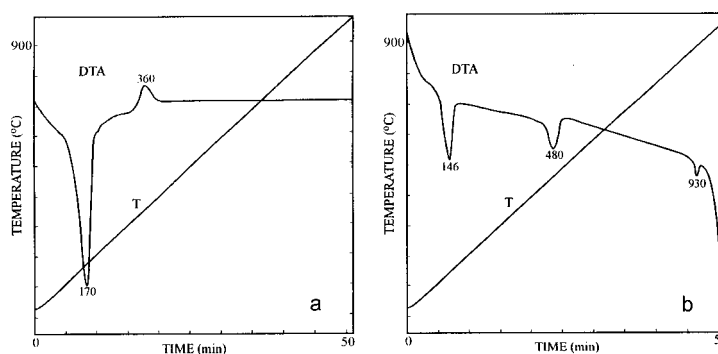| Product from	Peak maximum temperature/^oC			
	Endothermal reaction			Exotherm. reaction
1.0 M KCl	170	–	–	360
1.5 M KCl	128	478	930	–
2.0 M KCl	130	478	930	–
2.5 M KCl	129	475	920	–
3.0 M KCl	146	480	930	–
3.5 M KCl	145	460	920	–
4.0 M KCl	145	460	920	–

Fig. 2 DTA curves of products: a – in 1.0 M KCl solution, b – in 3.0 M KCl solution

Table 4 presents microscopic examination data on the products discussed in this paper.

As indicated in Table 4, the crystals produced in 1.0 M KCl solution differ from those of any other product, and are as described in the literature [2, 3] for the β-form of the hemihydrate and as indicated by the DTA data given above. The crystals of all of the other products (Table 4) are needle-shaped, very small, and quite different in length. The variation in crystal length may be explained by their being mixtures of $CaSO_4 \cdot 0.5H_2O$ and $K_2Ca_5(SO_4)_6 \cdot H_2O$ as primarily identified in X-ray analysis. α-$CaSO_4 \cdot 0.5H_2O$ is described [2, 3] as composed of clear needle-shaped crystals, but no description of $K_2Ca_5(SO_4)_6 \cdot H_2O$ crystals has been found in the literature. The presented data (Table 4) suggest needle-shaped crystals of the latter as well, in agreement with reference information [21] on a similar double salt ($Na_2SO_4 \cdot 5CaSO_4 \cdot 3H_2O$), which forms acicular crystals.

Table 4 Microscopic examination data on the product crystals

Product from	Crystal characters (shape, size, etc.)
1.0 M KCl solution	White, irregular, porous, brittle, tabular microcrystal aggregates; (Sample size and shape like those of raw selenite grain)
1.5–4.0 M KCl solutions	Single acicular crystals, colourless, clear, very small and unequal in length, which varies from 0.0162 to 0.0486 mm

The results of XRD, IR spectroscopic, DTA and microscopic examination show that the product obtained in 1.0 M KCl solution differs from those obtained in more concentrated KCl solutions (1.5–4.0 M).

β-$CaSO_4 \cdot 0.5H_2O$ is formed only in 1.0 M KCl solution, probably by selenite dehydration in the solid phase, because the solubility of selenite is too low to provide conditions for α-$CaSO_4 \cdot 0.5H_2O$ crystallization from this solution.

The more concentrated KCl solutions (from 1.5 M to 4.0 M) provide conditions (by higher selenite dissolution) for the crystallization of single needle-shaped α-$CaSO_4 \cdot 0.5H_2O$ crystals from solution, but also for the formation of $K_2Ca_5(SO_4)_6 \cdot H_2O$ from the reaction of KCl with $CaSO_4$.

Conclusions

The results obtained lead to the conclusion that the dehydration of solid selenite in the KCl solution with the lowest concentration (1.0 M) produces the β-form of the hemihydrate (β-$CaSO_4 \cdot 0.5H_2O$).

The α-form of the hemihydrate (α-$CaSO_4 \cdot 0.5H_2O$) is a product in more concentrated (from 1.5 M to 4.0 M) KCl solutions, mixed with $K_2Ca_5(SO_4)_6 \cdot H_2O$.

Evidently, pure α-hemihydrate cannot be produced by hydrothermal treatment of selenite in KCl solutions with concentrations of 1.5 M to 4.0 M. The question arises of the effect of $K_2Ca_5(SO_4)_6 \cdot H_2O$ on the properties of the α-hemihydrate product. The answer is expected from further study of the mechanical properties of the products.

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