

Phase diagram of the system $\text{CaSO}_4\text{—K}_2\text{SO}_4\text{—KNO}_3\text{—Ca(NO}_3)_2\text{—H}_2\text{O}$

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Abstract: Potassium nitrate as a fertilizer suitable for greenhouse and hydroponic applications can be prepared by the reaction of potassium sulphate with calcium nitrate. However, it may happen that simultaneously with the precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) also two other binary salts, viz. syngenite ($\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$) and görgeyite ($\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$) can crystallize. This would lower the yield of KNO_3 . For minimization of potassium loss we have to determine the conditions under which syngenite and görgeyite crystallize. As a useful tool for the quantitative determination of specific hydrates, simultaneous DTA/TG technique appeared. Each hydrate decomposes at a certain temperature. The loss of water at dehydration can be used for a quantitative determination of the amount of the hydrate in the precipitating solid phase.

Based on the experimental data several conclusions can be drawn: (i) excess of calcium cations lowers the concentration of sulphate ions in the liquid phase together with lowering of contents of syngenite and görgeyite in the solid phase; (ii) higher content of water results in a higher solubility of sulphate ions; (iii) joint crystallization of syngenite and gypsum occurs in the composition area interesting from the point of KNO_3 production; (iv) area of the primary crystallization of görgeyite does not exist in the phase diagram at 80 °C. However, görgeyite crystallizes at the molar ratio $\text{Ca(NO}_3)_2\text{:K}_2\text{SO}_4 = 1\text{:1}$ by ternary crystallization; (v) area of crystallization of pure gypsum is shifted to lower ratio $\text{Ca(NO}_3)_2\text{:K}_2\text{SO}_4$ by the addition of water to the system.

Keywords: görgeyite, phase diagram, potassium nitrate, syngenite

Introduction

Potassium nitrate is a fertilizer suitable for greenhouse and hydroponic applications. It is important that, for this application, KNO_3 has to be of purity higher than is usual for common fertilizers. Content of chlorides has to be lower than 0.6 %, content of calcium lower than 0.15 % (in the form of CaO). One of the ways how potassium nitrate of this purity can be prepared is the reaction:



This reaction seems simple. However, it may happen that simultaneously with the precipitation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) also two other binary salts, viz. syngenite ($\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$) and görgeyite ($\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$) can crystallize. This would lower the yield of KNO_3 . To avoid the crystallization of these undesirable substances, detailed knowledge of the phase diagram of the system $\text{CaSO}_4\text{—K}_2\text{SO}_4\text{—KNO}_3\text{—Ca(NO}_3)_2\text{—H}_2\text{O}$ is needed. Study of this phase diagram is the topic of presented contribution.

Phase diagram of the system $\text{CaSO}_4\text{—K}_2\text{SO}_4\text{—H}_2\text{O}$ was investigated by several researchers (Cameron

and Breazeale 1904; Cameron and Brown 1905; Clarke and Partridge 1934; Hill 1934; Voigt 2001; Yu and Mamoun 1989). Comprehensive review of this topic has been discussed recently (2003) by Freyer and Voigt. The authors concluded that the data on equilibria in this system are not reliable. The cited paper discusses also the influence of different electrolytes on the phase diagram in question. Unfortunately, the influence of nitrate, which is important for preparation of KNO_3 , is not discussed.

Based on the published papers (Cameron and Breazeale 1904; Cameron and Brown 1905; Clarke and Partridge 1934; Freyer and Voigt 2003; Hill 1934; Voigt 2001; Yu and Mamoun 1989) the following conclusions can be drawn:

1. Region of crystallization of syngenite $\text{K}_2\text{Ca(SO}_4)_2 \cdot \text{H}_2\text{O}$ diminishes with rising temperature and it disappears when the temperature reaches (180–190) °C.
2. Region of crystallization of görgeyite (called also pentasalt) $\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$ broadens with increasing temperature. At the temperature lower than 40 °C, görgeyite does not crystallize at all.

It can be assumed that the presence of nitrate in solution influences the stability regions of above

mentioned substances. However, the general trends will remain unchanged.

Equilibrium in a reciprocal system containing water at given temperature can be depicted in a tetrahedral, as shown schematically in Fig. 1.

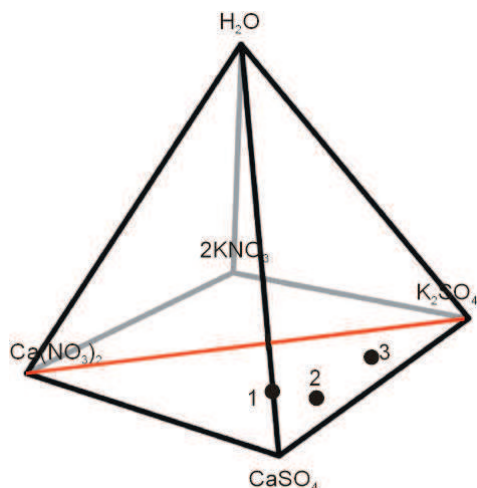


Fig. 1. Isotherm of the reciprocal system $\text{CaSO}_4\text{—K}_2\text{SO}_4\text{—KNO}_3\text{—Ca(NO}_3)_2\text{—H}_2\text{O}$. Points on a side plane correspond to following compounds: (1) gypsum, (2) görgeyite, (3) syngenite.

As mentioned above, for minimization of potassium loss it is necessary to determine the conditions under which syngenite and görgeyite crystallize. This is complicated by the fact that these phases are hydrates and they take also water from the solution. Thus, the solid-liquid equilibrium composition moves not along a line, but along a plane. At a con-

stant temperature we can meet not only secondary, but also tertiary crystallization.

For this reason, this study started with the determination of conditions under which the primary crystallization product consists only from gypsum. Investigated composition range was limited only to the diagonal $\text{K}_2\text{SO}_4\text{—Ca(NO}_3)_2\text{ (—H}_2\text{O)}$ because the primary interest was in the production of potassium nitrate. Content of water was close to the saturation of KNO_3 in the solution. In the second stage, the aim was to describe the regions of primary crystallization of gypsum, syngenite and görgeyite.

Experimental

Chemicals used: K_2SO_4 , p.a., Lachema Brno; $\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$, analytical reagent grade, Fisher; gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, precipitated for analysis, Merck; CaCl_2 was prepared from chemicals of p.a. purity.

Working procedure

$\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was weighed in 100 ml flask. Water necessary for its dissolution was added. Concentration of this solution was 63.8 wt. %. After reaching required temperature, hot K_2SO_4 solution (15 wt. %) was added. The flask was closed and the mixture was stirred for 1 h. Two temperatures were used: 80 °C and 100 °C, respectively. The solid product originating from reaction (1) was filtered off and dried 24 h at 55 °C in a dryer. (Filter cake was not washed.) Filter cake was weighed immediately after filtration and also after drying. Also the amount of liquid solution was weighed. The product was analysed by TG/DTA 6300, Perkin Elmer and by X-ray powder diffraction (STADI P, STOE).

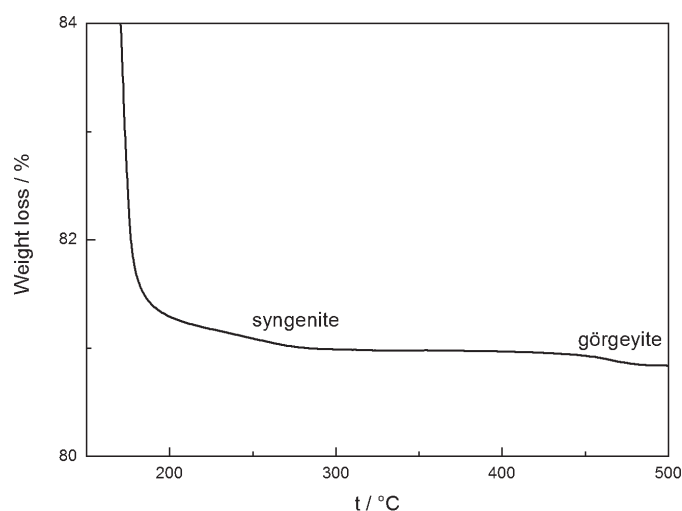


Fig. 2. TG record of a sample prepared at 100 °C.

Thermogravimetric Analysis

For using this method, it is important that the temperatures, at which the hydrates are losing water, are sufficiently different. In Fig. 2, typical thermogravimetric curve is shown. It is seen that gypsum loses water at (100–180) °C, while syngenite loses water at (200–300) °C and görgeyite at (400–500) °C. Losses of water of pure hydrates expressed in wt. % are summarized in Table 1. Loss of water from pure hydrates was determined from stoichiometry.

Tab. 1. Change in weight of pure hydrates at losing water.

	Weight loss [wt. %]	Temperature range [°C]
Gypsum	20.93	100–180 (200)
Syngenite	5.49	200–300
Görgeyite	2.06	400–500

The analysis of TG record makes it possible to determine quantitatively the presence of hydrates in the sample. Sum of weight of all present phases was in the interval (98.7–101.9) %, which characterizes precision of the method. Composition was then recalculated to 100 %. Error in the determination of hydrates is ± 0.6 %. Reproducibility of repeated measurements was ± 0.1 %.

Results and discussion

Influence of the ratio of calcium nitrate and potassium sulphate on the composition (especially presence of syngenite and görgeyite) of the solid

product which is in equilibrium with the solution was investigated. The experiments were carried out at 80 °C and 100 °C, respectively. After the crystallization of solid phase, the solution was saturated with potassium nitrate. The results are summarized in Figs.3 and 4. From the obtained results it follows that the increase of temperature results in diminishing the formation of syngenite (which is a desirable effect). On the other hand, the higher temperature favours formation of görgeyite. Loss of potassium at the formation of görgeyite is lower than at the formation of syngenite. Thus, higher temperature has a positive effect on the loss of potassium. Presence of nitrate ions in the solution limits the formation of both syngenite and görgeyite. When the excess of calcium nitrate with respect to stoichiometry of reaction (2) is 50 %, no syngenite is formed at 80 °C. Excess of 1 % of calcium nitrate completely hinders the formation of görgeyite at this temperature. At 100 °C, görgeyite is not formed if the excess of calcium nitrate is 25 %, while syngenite is not formed when the excess of calcium nitrate is as high as 40 %.



In the next series of experiments, the influence of nitrate on the crystallization of solid phases was studied in detail. These experiments were carried out at 80 °C. At this temperature, evaporation of water is lower than at 100 °C, and thus the precision in the determination of composition is higher. Molar ratio $n(\text{Ca}(\text{NO}_3)_2):n(\text{K}_2\text{SO}_4)$ was 1:1–3:1. The solution was either saturated with potassium nitrate or the saturated solution was diluted with 10 wt. % or

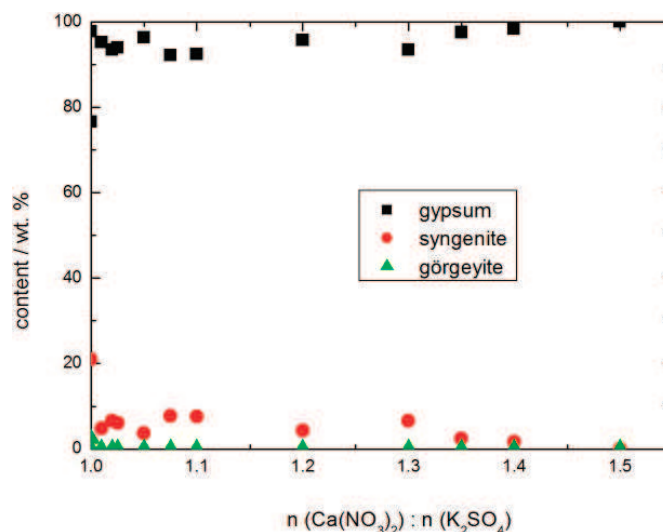


Fig. 3. Content of gypsum, syngenite, and görgeyite in the solid phase as a function of the ratio of calcium nitrate and potassium sulphate at 80 °C.

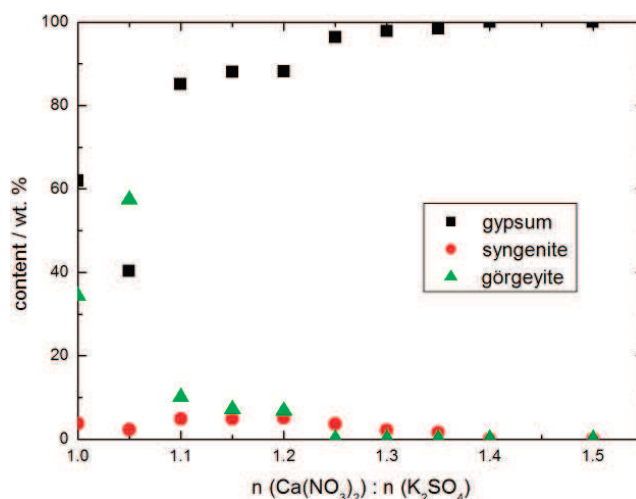


Fig. 4. Content of gypsum, syngenite, and görgeyite in the solid phase as a function of the ratio of calcium nitrate and potassium sulphate at 100 °C.

Tab. 2. Composition of the equilibrium solid and liquid phases (wt. %) as a function of composition. $t = 80\text{ °C}$.

Content of water	Molar ratio $\text{Ca}(\text{NO}_3)_2:\text{K}_2\text{SO}_4$	Composition of solid phase			Ionic composition of liquid phase				
		gypsum	syngenite	görgeyite	Ca^{2+}	2K^+	2NO_3^-	SO_4^{2-}	water
Saturated	1	0.766	0.15	0.008	0.002	0.034	0.057	0.000	0.906
	1.5	0.745	0	0	0.017	0.033	0.078	0.000	0.872
	2	0.849	0	0	0.028	0.031	0.098	0.000	0.843
	2.5	0.756	0	0	0.039	0.029	0.114	0.000	0.819
	3	0.876	0	0	0.047	0.026	0.125	0.000	0.802
Sat. + 10 %	1	0.930	0	0	0.000	0.032	0.051	0.000	0.917
	1.5	0.804	0	0	0.016	0.029	0.069	0.003	0.883
	2	0.741	0	0	0.029	0.027	0.085	0.003	0.856
	2.5	0.824	0	0	0.040	0.025	0.099	0.003	0.834
	3	0.720	0	0	0.042	0.024	0.112	0.000	0.822
Sat. + 20 %	1	0.944	0	0	0.002	0.028	0.044	0.005	0.921
	1.5	0.813	0.049	0	0.015	0.025	0.062	0.004	0.894
	1.2	0.677	0	0	0.008	0.027	0.051	0.005	0.909

20 wt. % of water. The results are summarized in Table 2 where the compositions of solid and liquid phases that are in equilibrium are shown. On the basis of this data the phase diagrams of the system $\text{CaSO}_4\text{—K}_2\text{SO}_4\text{—}2\text{KNO}_3\text{—Ca}(\text{NO}_3)_2\text{—H}_2\text{O}$ for different water contents were constructed (Fig. 5–7).

Based on the experimental data several conclusions can be drawn: (i) excess of calcium cations lowers the concentration of sulphate ions in liquid phase together with lowering of contents of syngenite and görgeyite in the solid phase; (ii) higher content of water results in a higher solubility of sulphate ions; (iii) joint crystallization of syn-

genite and gypsum occurs in the composition area interesting from the point of KNO_3 production; (iv) area of the primary crystallization of görgeyite does not exist in the phase diagram at 80 °C. However, görgeyite crystallizes at the molar ratio $\text{Ca}(\text{NO}_3)_2:\text{K}_2\text{SO}_4 = 1:1$ by ternary crystallization; (v) area of the crystallization of pure gypsum is shifted to lower ratio $\text{Ca}(\text{NO}_3)_2:\text{K}_2\text{SO}_4$ by the addition of water to the system.

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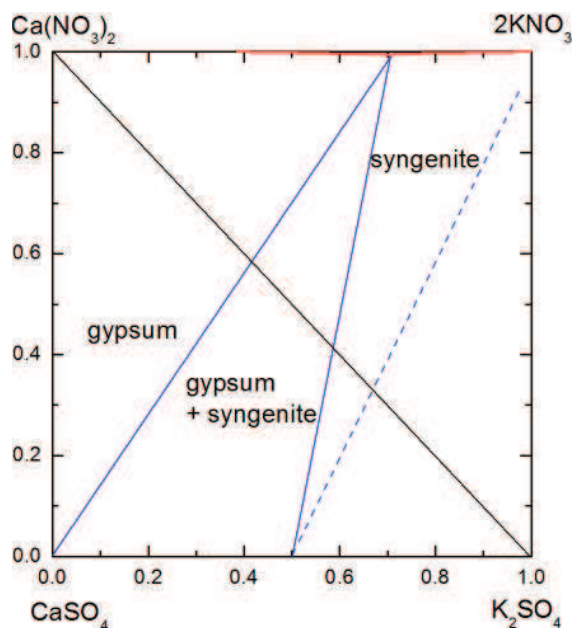


Fig. 5. Phase diagram of the system $\text{CaSO}_4\text{—K}_2\text{SO}_4\text{—}2\text{KNO}_3\text{—Ca(NO}_3)_2$ ($-\text{H}_2\text{O}$) in mass fractions. The liquid phase was saturated by KNO_3 .

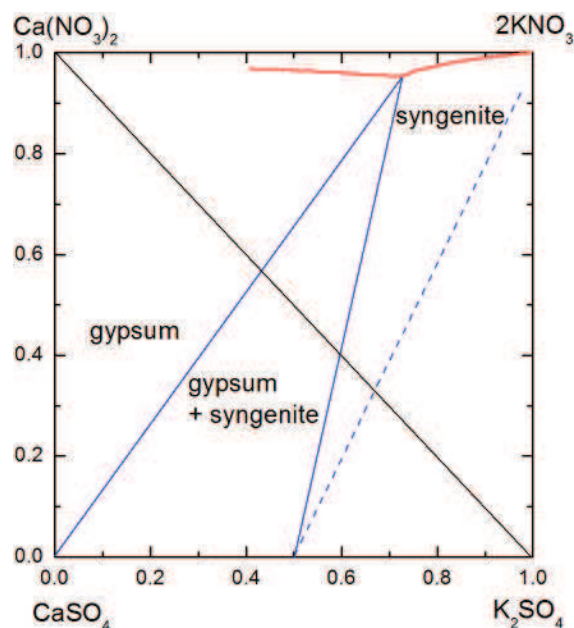


Fig. 6. Phase diagram of the system $\text{CaSO}_4\text{—K}_2\text{SO}_4\text{—}2\text{KNO}_3\text{—Ca(NO}_3)_2$ ($-\text{H}_2\text{O}$) in mass fractions. The liquid phase contained 10 wt. % of water excess with respect to KNO_3 saturation.

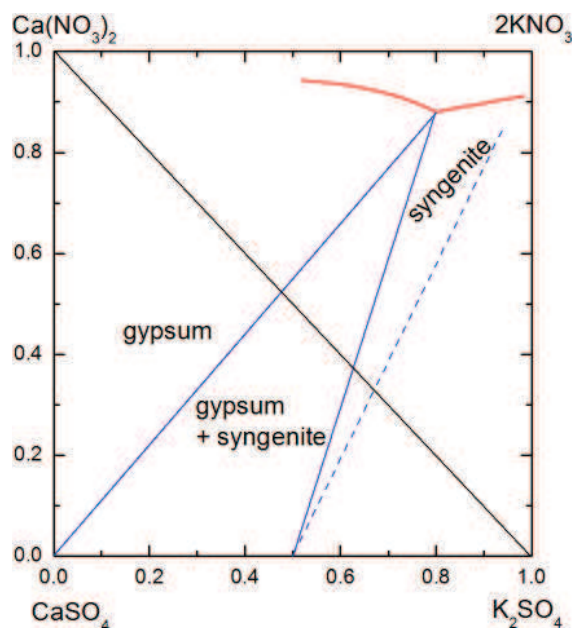


Fig. 7. Phase diagram of the system $\text{CaSO}_4\text{—K}_2\text{SO}_4\text{—}2\text{KNO}_3\text{—Ca(NO}_3)_2$ ($-\text{H}_2\text{O}$) in mass fractions. The liquid phase contained 20 wt. % of water excess with respect to KNO_3 saturation.

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