Original Article

Study Of The Solubility Diagram Of The System K^+, NH_4^+ // 1/2 SO_4^{-2} - H_2O At 25, 50, 75 And 100 ^0C

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Abstract

Annotation: Solubility in the system K^+, NH_4^+// 1/2 SO_4^{2-} – H_2O at 25, 50, 75 and 100^{0}C was studied by the isothermal method.. An isothermal diagram of solubility at 25, 50, 75 and 100^{0}C was constructed, on which the fields of crystallization of K_2SO_4, $(NH_4)_2SO_4$ and a new compound of the composition K_2SO_4•$(NH_4)_2SO_4$ are demarcated. The compound was isolated from the expected region of crystallization and identified by chemical and physicochemical analysis methods.

Keywords: potassium chloride, conversion, potassium nitrate, ammonium chloride, ammonium nitrate, technology, temperature, concentration

Introduction. Interest in the study of heterogeneous phase equilibrium is due to the practical application of the initial components.

Chlorine, along with fluorine, belongs to the group of halogens. However, fluorine exhibits more non-metallic (oxidizing) properties and therefore is a more aggressive and harmful impurity. According to agrochemical studies [1], the fluorine content in fertilizers up to 3% does not have a negative effect on plants. A similar value is adopted in most of the current standards for regulating the content of chlorine in non-chlorine fertilizers.

At the same time, improving the quality is one of the priorities in the development of the production of mineral fertilizers, and, according to Belarusian agrochemists, the chlorine content in fertilizers used in greenhouses should not exceed 1% [2-3].

The largest exporters of chlorine-free water-soluble complex fertilizers are Kemiro Agro (Finland), Norsk Hydro (Norway), Agrohanza (Poland), Buisky Chemical Plant OJSC (Russia), Nutri SI (Belgium), Haifa Chemicals and Israil Chemicals (Israel), Vicksburg Chemicals Co. (USA), SQM SA, PCS Ymbes SCM (Chile), The Arab Potash Compani Ltd (Jordan) [2].

According to published data on construction projects for the production of NPK fertilizers [2], during 1997-2000. the planned commissioning of new capacities for the production of potassium nitrate in the world amounted to over 474 thousand tons / year. The growth rate of the global market for chlorine-free water-soluble fertilizers is estimated at 4% per year.

Meanwhile, to date, a fairly large amount of research has been accumulated in the field of developing technological processes for obtaining various types of chlorine-free water-soluble complex fertilizers [3-11].

Materials and methods. The study of the solubility of salts by the isothermal method [12] was carried out by stirring the solutions of the studied compounds at a constant temperature with the preservation of a sufficient amount of solid phases in the mixture. The study was carried out in a therabolic flask with a stirrer placed in a thermostat, the temperature in which was maintained by a thermostat and a contact thermometer with an accuracy of ± 0.1 ^{0}C. After equilibrium was established, samples were taken from the liquid and solid phases for analysis, and the location of the figurative point of the system was determined.

Viewing images and obtaining elemental analysis of composite materials and coatings was carried out on a Zeiss SEM EVO MA (10) scanning electron microscope with x-act X-ray detector (Oxford Instrument Nano

Analysys). SEM consists of three main parts: a power supply, an electron-optical column with a sample chamber and an electron collector, and an image display system [13, 14, 15].

To determine the mineralogical composition, the diffraction patterns of heat treatment products were identified, which were recorded on a computer-controlled XRD-6100 apparatus (Shimadzu, Japan) [16, 17].

Results and discussion. In this regard, for the physicochemical substantiation of the process of obtaining chlorine-free complex nitrogen-potassium-sulfate fertilizers with a high content of nutrients, good physicochemical and mechanical properties, we studied and theoretically analyzed the isothermal method of the three-component system K^+, NH_4^+// 1/2 SO_4^{2-} – H_2O at 25, 50, 75 and 100ºC.

The equilibrium of the phases in the systems was established with continuous stirring and temperature control after 6-8 hours. Based on the chemical analysis of liquid and solid phases, and on the basis of the interpretation of literature data [18, 19], an isothermal diagram of the solubility of the studied systems at 25, 50, 75 and 100°C was constructed (Fig. 1).

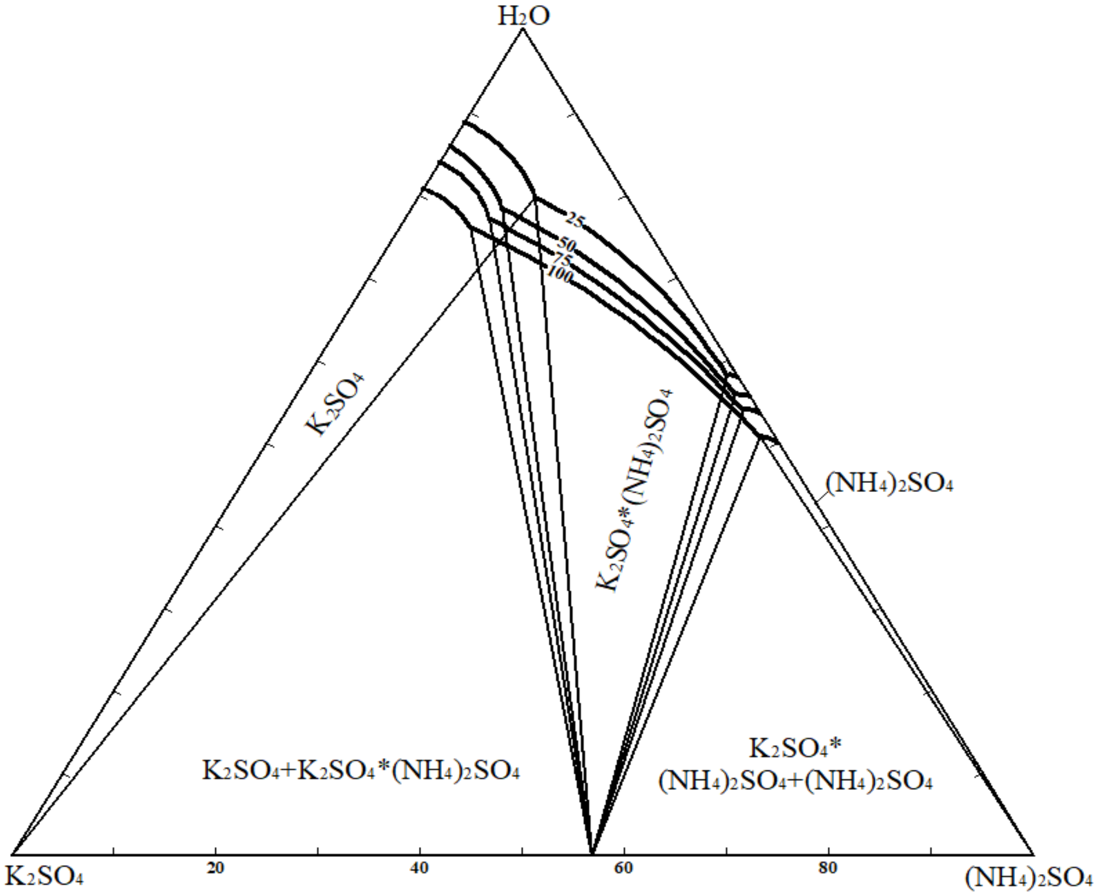

Figure 1. Isothermal diagram of solubility K^+, NH_4^+// 1/2 SO_4^{2-} – H_2O at 25, 50, 75 and 100^0C

Figure 1 presents data on solubility in the ternary system potassium sulfate - ammonium sulfate - water, which revealed that potassium sulfate in the presence of ammonium sulfate at 25, 50, 75 and 100 °C increases its solubility from 19.60, 21.62, 23.82 and 24.81%, respectively. While its initial solubility in water at the indicated temperatures was 10.75, 14.40, 17.10 and 19.40%. This is apparently due to complex formation in the system. Indeed, the liquidus curve of the solubility diagram splits into three branches, corresponding to the crystallization of two initial components – K_2SO_4, $(NH_4)_2SO_4$ and a compound of the composition K_2SO_4•$(NH_4)_2SO_4$.

The rectilinear rays emanating from the liquidus line of this compound intersect at a point located on the anhydrous side of the concentration triangle. This indicates that this compound does not contain water of crystallization.

The rays of the compound K_2SO_4•$(NH_4)_2SO_4$, connecting the pole of the complex with the origin of coordinates, cross the branch of its crystallization. This indicates the congruent solubility of the compound K_2SO_4•$(NH_4)_2SO_4$ in water without decomposition. Therefore, it can be recrystallized from aqueous solutions.

The compounds formed in the studied system were identified by chemical and physicochemical methods of analysis.

The chemical analysis of the solid phase isolated from the presumed crystallization region of $K_2SO_4 \cdot (NH_4)_2SO_4$ confirms its formation in the potassium sulfate – ammonium sulfate – water system.

Chemical analysis of the resulting compound gave the following results:

Found, %: K^+ -25.08; NH_4^- -10.39; SO_4^{2-}62.13.

For $K_2SO_4 \cdot (NH_4)_2SO_4$ calculated,: K^+ -25.49; NH_4^- -11.77; SO_4^{2-}62.74.

The X-ray diffraction pattern of the $K_2SO_4 \cdot (NH_4)_2SO_4$ compound has individual sets of diffraction reflections, diffraction line intensities, and reflection angles that are not characteristic of the initial components (Figure 2).

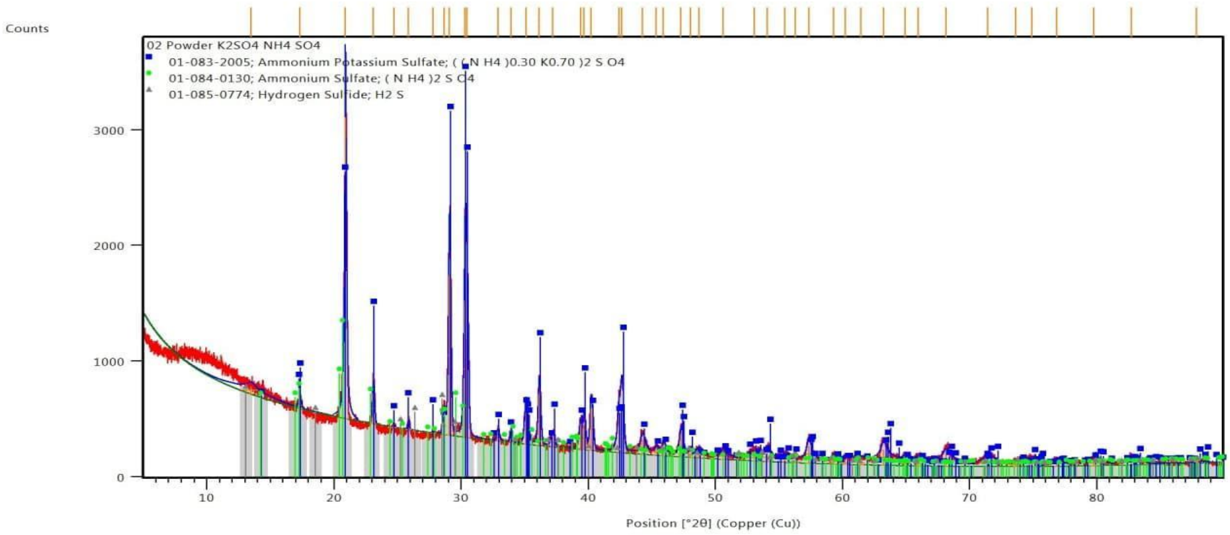

Figure 2. X-ray pattern of the compound $K_2SO_4 \cdot (NH_4)_2SO_4$

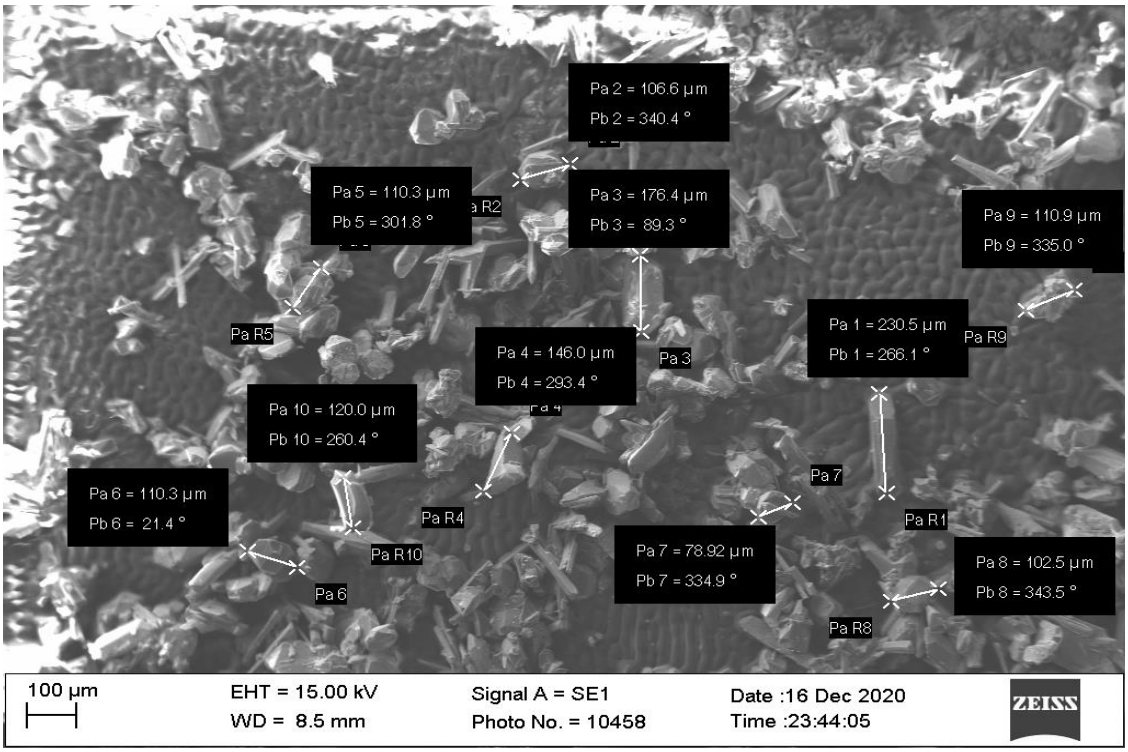

Figure 3. Morphological studies and particle sizes of the compound $K_2SO_4 \cdot (NH_4)_2SO_4$

According to the data obtained, the length of the compound particles reaches up to P_{a4}-1.627 mm, in the studied ranges of variation of technological parameters, large prismatic crystals of potassium nitrate with a size of Lxhxb-0.125:1.627 x 0.1-0.5 x 0.1-0.3 mm are formed.

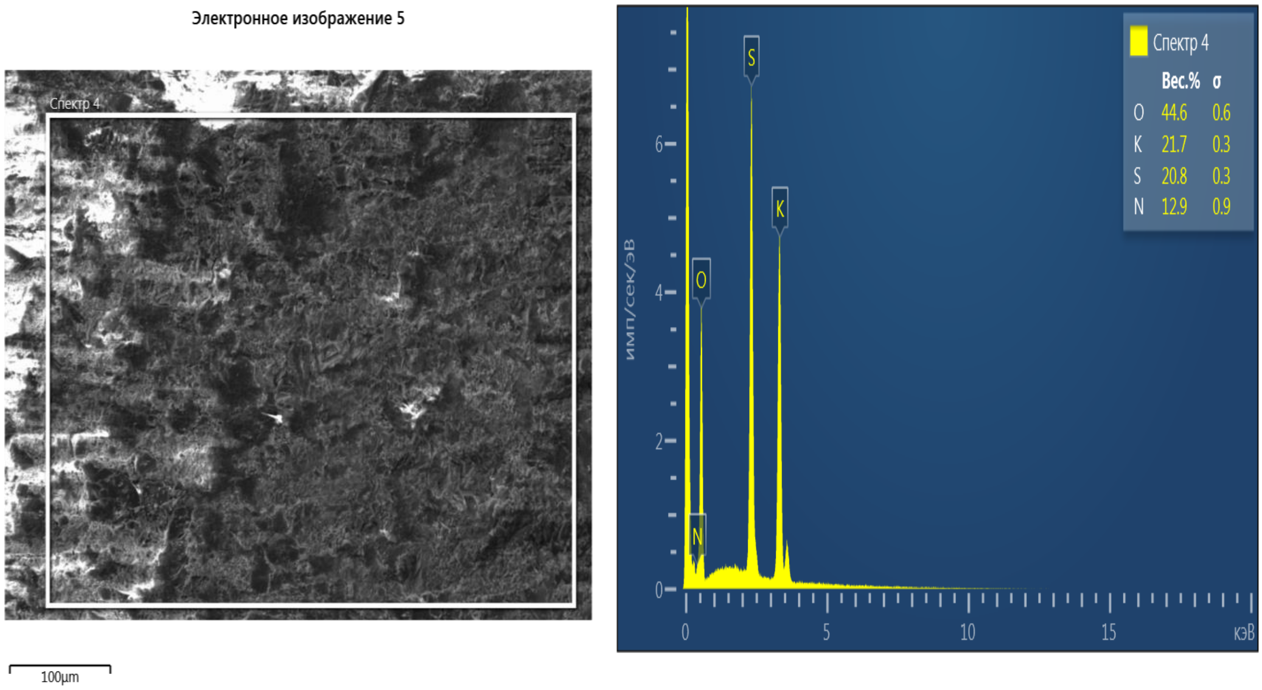

Figure 4. Energy-dispersive spectrum of the compound K_2SO_4•$(NH_4)_2SO_4$

Table

Energy-dispersive spectrum of the compound K_2SO_4•$(NH_4)_2SO_4$

Compound	Element	The weight.%	Sigma Weight.%	Standard name
K_2SO_4•$(NH_4)_2SO_4$	N	12.92	0.92	SiO_2
	O	44.57	0.59	Al_2O_3
	S	20.81	0.29	SiO_2
	K	21.70	0.31	Cu
	Sum:	100.00		

It follows from the table that the elemental composition of K_2SO_4•$(NH_4)_2SO_4$ has the following chemical composition (wt %): N, 12.92; O, 44.57; S, 20.81; K - 21.70. According to elemental analysis, the sample corresponds to the compound formed.

Conclusion. Solubility in the system K^+, NH_4^+// 1/2 SO_4^{2-} – H_2O at 25, 50, 75 and 100^0C was studied by the isothermal method. An isothermal diagram of solubility at 25, 50, 75 and 100^0C was constructed, on which the fields of crystallization of K_2SO_4, $(NH_4)_2SO_4$ and a new compound of the composition K_2SO_4•$(NH_4)_2SO_4$ are demarcated. The compound was isolated from the expected region of crystallization and identified by chemical and physicochemical analysis methods.

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