STUDYING THE SOLUBILITY OF THE SYSTEM $ZnSO_4$ - KNO_3 - H_2O

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ABSTRACT

The solubility of the components in the $ZnSO_4$ - KNO_3 - H_2O system was studied by the visual-polythermal method in the temperature range from -7.0°C to 42.0°C. The phase diagram delimits the fields of ice crystallization, KNO_3, $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$, and $ZnSO_4$. A solubility diagram was constructed, and a new compound $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$ was separated. The new compound was identified by chemical, X-ray phase, thermogravimetric, and IR spectroscopic analysis.

Keywords: potassium nitrate, zinc sulfate, potassium-zinc sulfate hexahydrate, visual polytherm, X-ray phase analysis, IR spectrum, thermogravimetric analysis.

INTRODUCTION

The interest in studying the solubility in the $ZnSO_4$ - KNO_3 - H_2O system is related to the practical importance of the components of microelement fertilizers for agriculture.

Trace elements [1, 2] have an important role in the environment and the health of plants, animals and people [3 - 6]. Among microelements, the importance of zinc for the life cycle of plants and humans is incomparable [7 - 9]. Millions of hectares of agricultural land and one-third of the world's population suffer from zinc deficiency [10 - 13]. One of the methods successfully used in the fight against zinc deficiency is the use of zinc-containing fertilizers [14]. Using trace elements in fertilizers can eliminate the deficiency of microelements necessary for the normal growth of plants [15]. Many sources of micronutrients are used together with N-P-K fertilizers, thus micronutrient deficiency [16, 17] in the soil is eliminated by using micronutrients together with fertilizers [18, 19]. The application of zinc sources with nitrogen fertilizers is effective due to the acidic effect of the fertilizers on the soil, but varies according to the fertilizer pH [20]. The effects of zinc fertilizers on the growth and yield of many plants such as alfalfa, wheat, corn, barley, cotton, and potato were investigated in numerous scientific types of research. At the same time, an increase in the productivity of these plants was observed [21]. Application of NPK fertilizers enriched with micronutrients provides comprehensive benefits such as increased grain yield and improved nutritional quality of harvested grains. The reason for improving the nutritional quality of grain is those micronutrient-enriched NPK fertilizers also increase the concentration of micronutrients in grain [22]. In the future, by paying special attention to the micronutrient status of soil and plants, it is possible to grow healthy crops and further increase soil fertility, especially in developing countries [23].

To solve the problem of producing highly effective, complex NPK fertilizers, deep physicochemical studies of the interaction of microelements with fertilizer components in the process of their production, storage and the establishment of the mechanism of influence of additives on the properties of the resulting products are required. For the purpose of physical and chemical substantiation of the process of obtaining NPK fertilizers containing, depending on the ratio of $N:P_2O_5:K_2O$ and solubility in water, potassium chloride, potassium and ammonium sulfates, monoammonium phosphate, urea or ammonium nitrate, the interaction of potassium nitrate was studied. In order to identify the possibility the use of zinc-containing wastes and middling of non-ferrous metallurgy, as well as the chemical industry in the production of mineral fertilizers with the addition of the trace element zinc, the solubility of components in the $ZnSO_4$ - KNO_3 - H_2O system was studied visually by the polythermal method in the temperature range from -7.0°C to 42.0°C.

EXPERIMENTAL

Water, potassium nitrate, and zinc sulfate are the objects of research. In our research, we used chemically pure potassium nitrate (GOST 4217-77) and zinc sulfate salt (GOST 4174-77). Our experimental measurements included X-ray phase analysis (LabX XRD-6100, Japan) [24], Infrared spectroscopic analysis (Specord IR-75) [25], and thermal analysis (DTG-60, Japan). The research employed the visual-polythermal method [27] using a TN-6 glass mercury thermometer with a measurement range of -30°C to 60°C, as well as the pycnometric method (GOST 31992.1-2012) [28]. The content of potassium-zinc sulfate hexahydrate was determined by elemental analysis for potassium, zinc, hydrogen, and sulfur was carried out according to (Zeiss EVO MA10) [29]. A VPZh viscometer was used to measure the viscosity of the solutions, and a FE20 METTLER TOLEDO pH meter was used to measure the pH value of the solutions.

RESULTS AND DISCUSSION

The solubility and properties of the components of the $ZnSO_4$ - KNO_3 - H_2O system at different temperatures and concentrations were studied to demonstrate the physico-chemical interactions between zinc sulfate and potassium nitrate.

The $ZnSO_4$ - KNO_3 - H_2O system was studied using thirteen internal sections (Fig. 1). Of these, sections I-V were studied from the side of $ZnSO_4$ to the peak of KNO_3, and sections VI-XIII from the side of KNO_3 - H_2O to the peak of $ZnSO_4$. Based on binary systems and internal sections, a polythermal solubility diagram of the $ZnSO_4$ - KNO_3 - H_2O system was constructed in the temperature range from -7.0°C to 42.0°C. On the phase diagram of the state of the system, the fields of ice crystallization, potassium nitrate, $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$, and zinc sulfate are delimited. These fields converge at three triple points of the system. The equilibrium composition of solutions at the double and triple points of the system and the corresponding crystallization temperatures were determined (Table 1). The first triple point corresponds to 9.7 % potassium nitrate, 5.0 % zinc sulfate, and 85.3 % water with a crystallization temperature of -5.0°C. In this case, the solid phase will consist of potassium nitrate, ice, and potassium-zinc

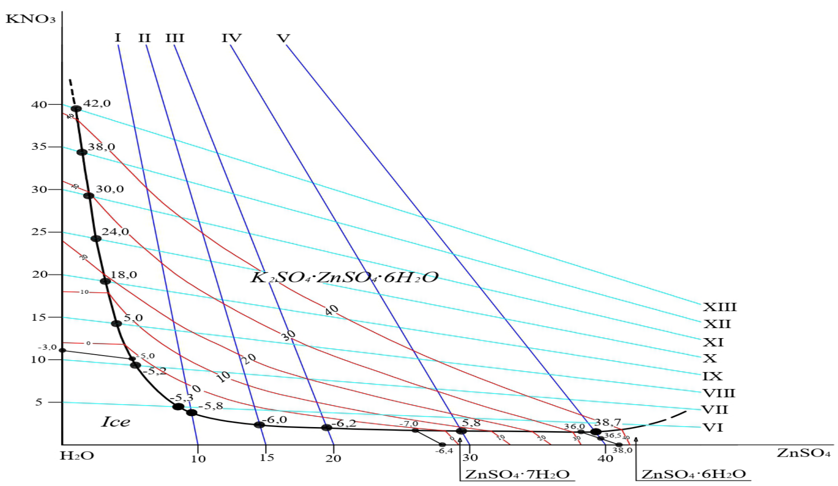

Fig. 1. Solubility polytherm of the $ZnSO_4$ - KNO_3 - H_2O system.

sulfate hexahydrate.

The second triple point corresponds to 1.7 % potassium nitrate, 26.0 % zinc sulfate, and 72.3 % water with a crystallization temperature of -7.0°C. The composition of the solid phase consists of ice, zinc sulfate heptahydrate, and potassium-zinc sulfate hexahydrate.

The third triple point corresponds to 1.6 % potassium nitrate, 39.5 % zinc sulfate, and 58.9 % water with a crystallization temperature of +36.0°C, the composition of the solid phase consists of zinc sulfate heptahydrate, zinc sulfate hexahydrate, and potassium-zinc sulfate hexahydrate.

On the polythermal diagram, the solubility isotherms of the system are expressed at 0°C, 10°C, 20°C, 30°C, and 40°C. The results obtained show that a new phase, the $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$ compound, has formed in the system. To identify a new compound in the system, physico-chemical analyzes were carried out, (X-ray phase, IR spectroscopic, and thermal analyses).

Changes in viscosity, density, pH, and crystallization temperature were studied by initially preparing 0.01M solutions of $ZnSO_4$ and KNO_3 components. To establish the possible course of the reaction in the $ZnSO_4$ - KNO_3 - H_2O system, changes in the indicators of viscosity characteristics, pH, and crystallization temperature of a mixture of various ratios of 0.01 M solutions of potassium nitrate and zinc sulfate were determined.

Analysis of the data obtained, the ratio of components - pH 0.01 M solutions shows that, with an increase in the proportion of 0.01 M solution of potassium nitrate from 3 mL to 30 mL and decrease the content of a 0.01 M solution of zinc sulfate from 30 mL to 0 mL, the pH value increases from 3.84 to 5.33. Up to a ratio of 15:15, the pH value of the mixtures increases along the curve, then it can be seen that the pH value increases again as the amount of potassium nitrate in the mixture increases. The linear dependence of pH indicates an increase in pH values in proportion to the increase in the proportion of potassium nitrate since the pH of 0.01 M potassium nitrate is higher than that of 0.01 M zinc sulfate (Fig. 2).

The crystallization temperature of 0.01 M $ZnSO_4$ solution increases from -1°C to 0°C, correspondingly, with the increasing proportion of KNO_3 solution.

Table 1. Double and triple nodal points of the $ZnSO_4$ - KNO_3 - H_2O system.

Composition of the liquid phase , %			Crystallization temperature, °C	Solid phase
KNO_3	$ZnSO_4$	H_2O		
39.6	0.9	59.5	+42.0	$KNO_3 + K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
34.4	1.2	64.4	+38.0	$KNO_3 + K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
29.4	1.9	68.7	+30.0	$KNO_3 + K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
24.2	2.5	73.3	+24.0	$KNO_3 + K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
19.4	3.2	77.4	+18.0	$KNO_3 + K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
14.3	4.1	81.6	+5.0	$KNO_3 + K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
10.9	-	89.1	-3.0	ice + KNO_3
9.7	5.0	85.3	-5.0	ice + $KNO_3 + K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
9.5	5.3	85.2	-5.2	ice + $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
4.7	8.4	86.9	-5.3	ice + $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
3.9	9.6	86.5	-5.8	ice + $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
2.3	14.6	83.1	-6.0	ice + $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
2.0	19.5	78.5	-6.2	ice + $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
-	28.0	72.0	-6.4	ice + $ZnSO_4 \cdot 7H_2O$
1.7	26.0	72.3	-7.0	ice + $ZnSO_4 \cdot 7H_2O$ + $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
1.6	29.3	69.1	+5.8	$ZnSO_4 \cdot 7H_2O$ + $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
1.6	39.5	58.9	+36.0	$ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot 6H_2O$ + $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$
0.9	39.8	59.3	+36.5	$ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot 6H_2O$
-	40.9	59.1	+38.0	$ZnSO_4 \cdot 7H_2O + ZnSO_4 \cdot 6H_2O$
1.8	39.7	58.5	+38.7	$ZnSO_4 \cdot 6H_2O + K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$

Table 2. Changes in the physico-chemical properties of solutions depending on the composition of the components in the system [$ZnSO_4$ (0.01 M)] and [KNO_3 (0.01 M)].

№	Composition of components		pH	Density g cm^{-3}	Viscosity	Crystallization temperature
	$ZnSO_4$, ml	KNO_3, mL				
1	30	0	3.84	0.98458	0.955	-1.0
2	27	3	4.36	0.98405	0.952	-1.1
3	24	6	4.52	0.98356	0.950	-1.2
4	21	9	4.60	0.98320	0.945	-1.3
5	18	12	4.68	0.98300	0.938	-1.2
6	15	15	4.69	0.98292	0.933	-1.0
7	12	18	4.76	0.98290	0.932	-0.9
8	9	21	4.86	0.98283	0.931	-0.8
9	6	24	4.98	0.98282	0.929	-0.7
10	3	27	5.14	0.98272	0.925	-0.6
11	0	30	5.33	0.98224	0.924	0

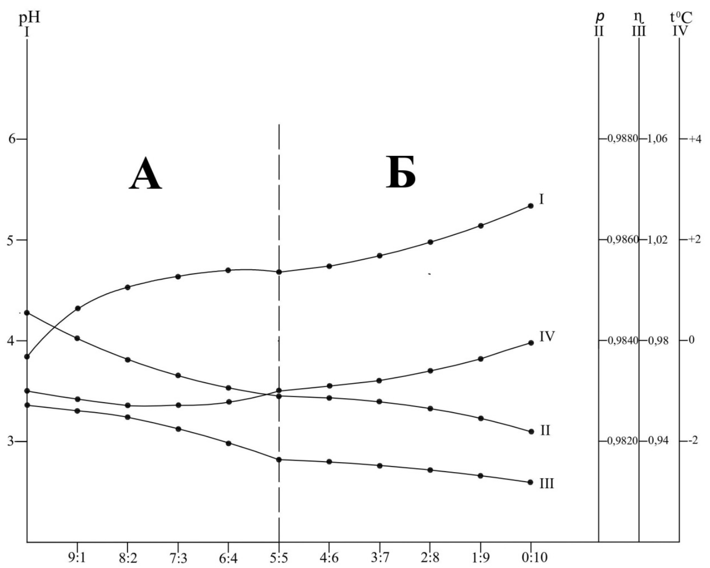

Fig. 2. Changes in pH (1), density (2), viscosity (3) and crystallization temperature (4) of solutions depending on the composition of components in the $ZnSO_4$ - KNO_3 - H_2O system.

Viscosity with an increase in the content of 0.01 M solutions of potassium nitrate in the mixture and a decrease in zinc sulfate decreases linearly from 0.955 mm^2 s^{-1} to 0.924 mm^2 s^{-1} and also decreases to 0.933 mm^2 s^{-1}, having a fracture at a ratio of components 1:1.

Chemical analysis of the new compound gave the following results: found, mass. %: K = 17.2; Zn = 14.5; S = 14.3; O = 50.2; H = 2.69; For $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$ calculated, mass. %: K = 17.6; Zn = 14.6; S = 14.4; O = 50.5; H = 2.7.

In order to confirm the individuality of the obtained compound, analysis using modern physico-chemical analysis methods was carried out.

Thermal analysis of the $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$ compound was carried out in the temperature range of 0°C - 1000°C for 90 minutes. Six endothermic and one exothermic effect were noticed. It can be seen that they correspond to the endothermic effects at 103.93°C, 139.09°C, 318.85°C, 493.37°C, and 752.18°C and the exothermic effects at 253.54°C. With increasing

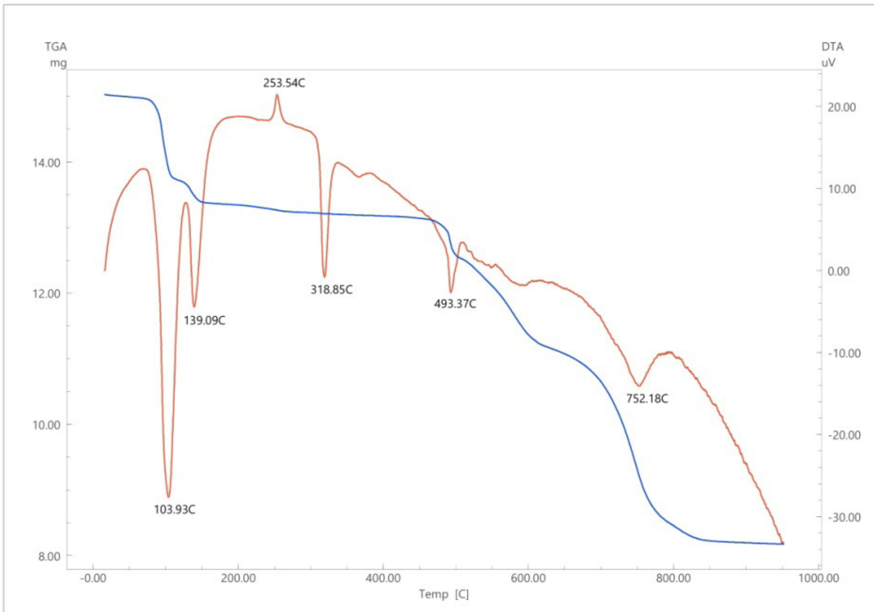

Fig. 3. Derivatogram of the compound $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$.

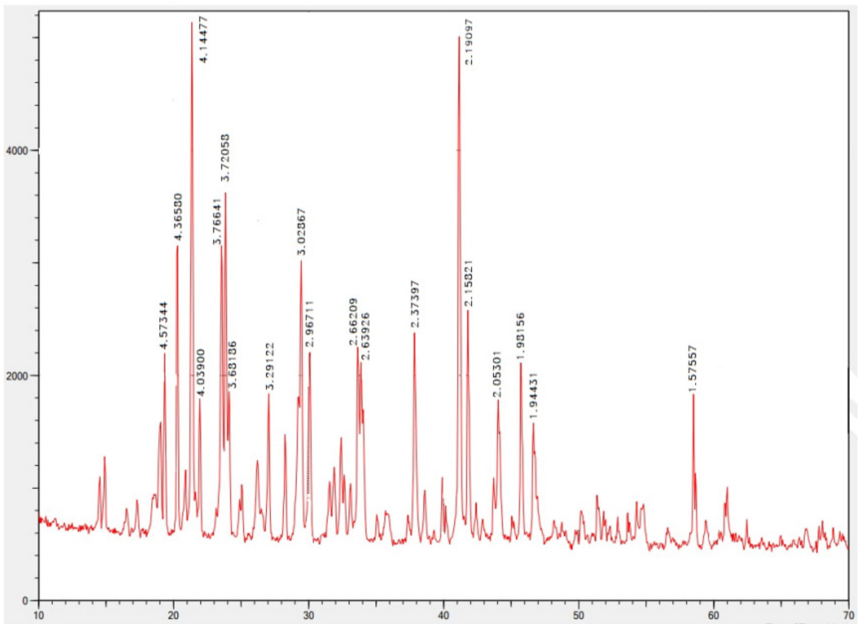

Fig. 4. X-ray phase analysis of $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$.

temperature, the decomposition of the initial substance was 19.275 % at 103.93°C and 55.663 % at 752.18°C. It can be seen that the initial loss was due to the evaporation of water in the crystal composition and the subsequent loss was due to sulfur oxides. In the temperature range from 752.18°C to 1000°C, almost no loss was observed due to the presence of ZnO and K_2O compounds (Fig. 3).

As can be seen from the X-ray phase analysis (Fig. 4), all the changes in the diffractograms, as well as the activation of their reflection angles, the set of interplanar distances and the diffraction lines confirm that the new compound is $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$.

When observing the IR spectrum of the $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$ crystal structure, it can be seen that water is strongly connected with hydrogen bonds in the region of 1400 - 1700 cm^{-1}. The 3167.12 cm^{-1} part of the band represents the stretching vibration of the H-bonded O-H group, and the frequency range of 2358.94 cm^{-1} in the middle part represents the stretching vibration of the free O-H group. The following peaks of

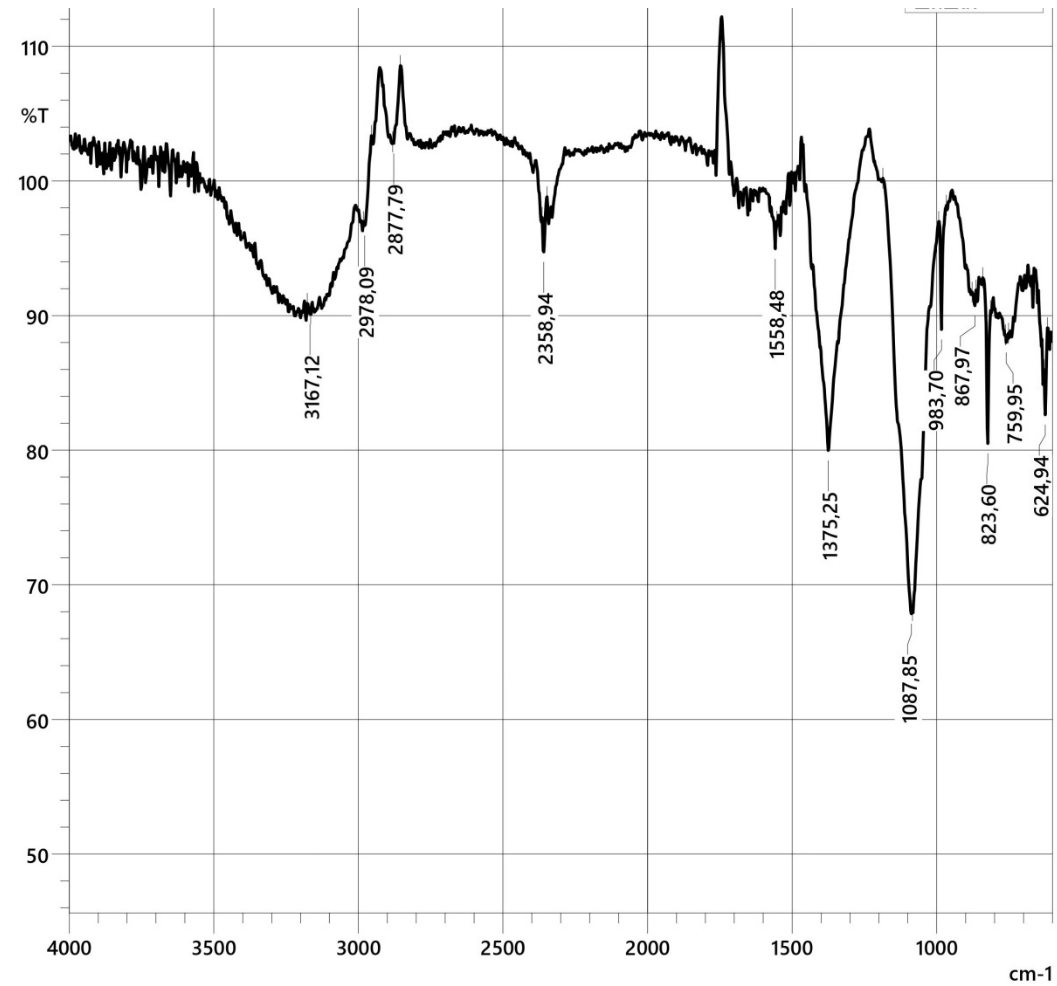

Fig. 5. FTIR spectrum of $K_2SO_4 \cdot ZnSO_4 \cdot 6H_2O$

the band, including 1087.85 cm^{-1} asymmetric stretching, 983.70 cm^{-1} symmetric stretching, and 624.94 cm^{-1} bending mode vibrations indicate that they belong to the SO_4^{-2} group. The frequency ranges of 2000 - 2400 cm^{-1} in the middle width of the band represent the stretching vibration of the free O-H group and 1558.48 cm^{-1} the bending vibration of the H-O-H group (Fig. 5). Descriptions of the given IR spectra confirm that the new compound is potassium-zinc sulfate hexahydrate.

CONCLUSIONS

According to the change in the solubility of the components and the physico-chemical properties of the solutions (density, viscosity, crystallization temperature, pH), the optimal conditions for obtaining the potassium-zinc sulfate hexahydrate compound in the above-mentioned system were determined. Separated potassium-zinc sulfate hexahydrate was analyzed based on physico-chemical analysis. In future studies, zinc formaldehyde and ammonium nitrate will be examined for their solubility and interaction.

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