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Production and Properties of Double Potassium-Ammonium Sulfate

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Abstract—Process in which double potassium-ammonium sulfate is produced from potassium chloride and sulfuric acid was studied. A thermal analysis of the compound KNH_4SO_4 was made and the melting and decomposition points of double potassium-ammonium sulfate were determined. An X-ray phase analysis revealed the processes occurring when double potassium-ammonium sulfate is calcined at temperatures of 330, 370, and 580°C. The chemical processes in which double potassium-ammonium sulfate decomposes to give ammonium hydrosulfate were examined.

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A topical issue in the technology of mineral fertilizers is the manufacture of integrated fertilizers. A chlorine-free nitrogen-potash fertilizer, double potassium-ammonium sulfate KNH_4SO_4 , is promising in this regard. It contains potassium and ammonium ions and sulfate ions at a useful component ratio $\text{N} : \text{K}_2\text{O} : \text{S} = 1 : 6.7 : 2.3$. This compound has no chlorides and nitrates that can adversely affect the growth and development of plants.

The compound KNH_4SO_4 is poorly studied and published data on its properties and production methods are hardly available. In the present study, we examined the method for obtaining potassium-ammonium sulfate by conversion of potassium chloride with sulfuric acid and subjected the product obtained to thermal and X-ray phase analyses.

The goal of the study was to obtain double potassium-ammonium sulfate, find processes occurring when this compound is exposed to high temperatures, and determine products formed in this case. It is necessary to examine the effect of temperature on the KNH_4SO_4 substance under study to determine whether the double salt can be decomposed into potassium and ammonium sulfates and determine the conditions of this process. In addition, the stability of the double potassium-ammonium sulfate under heating is important for studying the drying process of the finished fertilizer.

Potassium-ammonium sulfate can be obtained via conversion of potassium chloride with sulfuric acid, followed by neutralization of the resulting hydrosulfate with ammonia by the reactions [1, 2]



To obtain KNH_4SO_4 in laboratory conditions, we used a potassium chloride solution with concentration of 24.5%, concentrated sulfuric acid (92%) and ammonia solution (25% NH_3). The potassium chloride solution was prepared from flotation potassium chloride and distilled water at $\text{S} : \text{L} = 1 : 3$. Potassium chloride was converted with sulfuric acid by reaction (1) in a reactor at a constant agitation speed of 600 rpm at a temperature of 120°C. Hydrogen chloride (HCl) vapor was removed from the reactor with water vapor and condensed in the reflux. It was experimentally determined that the conversion is as high as 98% at conversion process duration of 2 h. The obtained potassium hydrosulfate solution was cooled to room temperature under permanent agitation at a rate of 600 rpm. In the process, crystals of potassium hydrosulfate precipitated. The resulting crystalline potassium hydrosulfate (KHSO_4) was filtered-off and placed in another reactor with an ammonia solution,

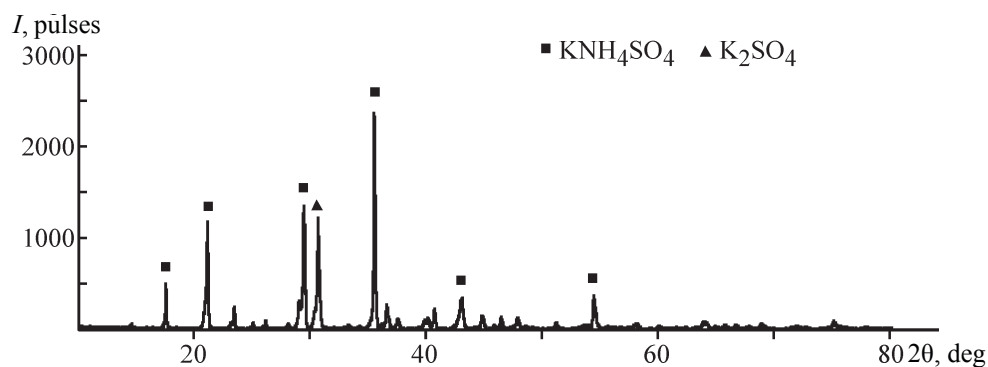


Fig. 1. X-ray diffraction pattern of the product obtained upon neutralization. (*I*) Intensity and (*2θ*) Bragg angle; the same for Fig. 3.

in which potassium hydrosulfate was neutralized in accordance with reaction (2). The neutralization was performed at room temperature (25°C) under agitation in the course of 1 h. The resulting crystals of double potassium-ammonium sulfate were dried at 110°C to constant mass.

In this study, we made an X-ray phase analysis of the product obtained as described above. The analysis was performed on a Shimadzu XDR7000 installation, which is a compact general-purpose X-ray diffractometer with a vertical goniometer. A prepared powder of the substance under study was placed in a cuvette mounted sample-upwards in the goniometer holder. The measurements were made at angles in the range 10–100° and recording rate of 2 deg min⁻¹. The anode was made of copper. An X-ray diffraction pattern of the sample is shown in Fig. 1.

The X-ray phase analysis demonstrated that the main reflections obtained when measuring the substance under study correspond to double potassium-ammonium sulfate. The product also contains potassium sulfate. The compounds represented in the X-ray diffraction pattern (KNH₄SO₄, K₂SO₄) have the crystal lattice of arcanite. A chemical analysis demonstrated that the resulting double potassium-ammonium sulfate contains 97.2% main substance (KNH₄SO₄) and admixtures of unreacted potassium hydrosulfate KHSO₄ and by-products, such as sodium and potassium sulfates (Na₂SO₄, K₂SO₄) and potassium, sodium, and ammonium chlorides (KCl, NaCl, NH₄Cl). The compound with this degree of purity can be used as fertilizer.

A thermal analysis of KNH₄SO₄ was made with a Netzsch STA 449C device for synchronous thermal analysis (Germany). Al₂O₃ served as reference. The measurements were made in air at a heating rate of 10 deg min⁻¹. A sample with a certain mass (5 mg)

was placed in a crucible mounted in the thermobalance holder situated in the furnace of the device. The heating was performed by a prescribed temperature program. When the sample was heated, the integral (TG) curve describing the loss of mass as a function of temperature and the differential (DSC) curve of heat effects relative to the reference sample were recorded. A thermogram of the sample of double potassium-ammonium sulfate is shown in Fig. 2.

An analysis of the thermogram (Fig. 2) on the basis of the change in mass in the TG curve suggests that double potassium-ammonium sulfate starts to decompose at a temperature of 223°C. The first minor endothermic peak in the DSC curve at *T* = 229.4°C corresponds to the melting of double potassium-ammonium sulfate. Also, the DSC curve shows in the decomposition of double potassium-ammonium sulfate two endothermic effects and one exothermic effect. To the endothermic effect at *T* = 332.1°C corresponds the 9.74% loss of mass by the sample of double potassium-ammonium sulfate, overlapped by the exothermic effect at *T* = 369.6°C, which characterizes the recrystallization of the decomposition process. To the endothermic peak at *T* = 580.1°C corresponds the 12.15% loss of mass.

To examine the processes and the resulting substances, we performed a number of experiments in which the double potassium-ammonium sulfate was calcined at 330, 370, and 580°C. For this purpose, a 1-g sample of KNH₄SO₄ in a porcelain boat was placed in a tubular furnace and calcined at a prescribed temperature for 1 h, with air purge. The evolving gas was absorbed with water containing an acidity indicator, Methyl Orange. The gravimetric method was used to measure the loss of mass by a KNH₄SO₄ sample due to the evolution of a gas. On performing the calcination, we made an X-ray phase

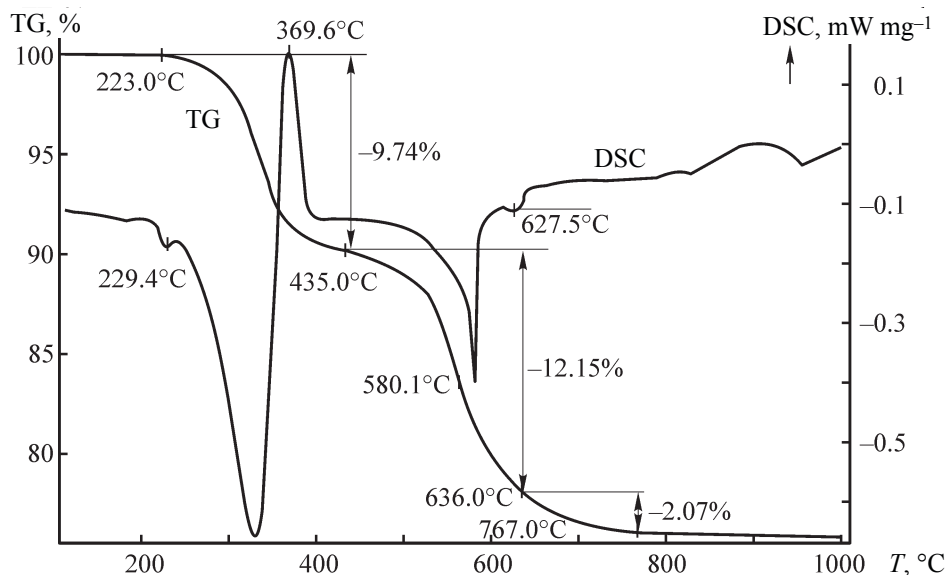


Fig. 2. Thermogram of double potassium-ammonium sulfate. (*T*) Temperature.

analysis of samples of the resulting substances. The data obtained are presented in the table and Fig. 3.

To exclude the influence exerted by diffusion in the course of calcination of double potassium-ammonium sulfate in the furnace, we used a small weighed portion (1 g) of the substance under study. An X-ray phase analysis of the product obtained in calcination of double potassium-ammonium sulfate at 330°C (Fig. 3a) demonstrated that the main phases contained in the product are potassium sulfate (K_2SO_4) and ammonium hydrosulfate (NH_4HSO_4).

It follows from an analysis of the X-ray diffraction pattern that double potassium-ammonium sulfate decomposes by the reaction



Based on the results of the X-ray phase analysis and on a comparison of the possible, calculated by reaction (3), amount of released ammonia with the loss of mass by the sample calcined at 330°C (see table), we can

conclude that ammonium sulfate contained in KNH_4SO_4 fully decomposes into potassium sulfate, ammonium hydrosulfate, and ammonia.

As the endothermic effect develops beginning at 332.1°C, an exothermic effect appears at 369.6°C, which may be due to the oxidation of the released ammonia or to the recrystallization of sulfates contained in the KNH_4SO_4 compound. Based on published data [3], we found that ammonia is slowly oxidized in the absence of a catalyst even in the temperature range 400–600°C. Therefore, the oxidation of ammonia at 369.6°C is unlikely, and the exothermic effect at this temperature (Fig. 1) is due to the recrystallization of sulfates. When double potassium-ammonium sulfate is calcined at 370°C, the main phases contained in the product are potassium sulfate (K_2SO_4), ammonium hydrosulfate (NH_4HSO_4), and potassium pyrosulfate ($K_2S_2O_7$), which is confirmed by the X-ray diffraction pattern in Fig. 3b).

Potassium sulfate is a substance that is stable by virtue of its nature and has a melting point of 1069°C [3].

Loss of mass by a sample and qualitative composition of gases and vapors released in calcination

Calcination temperature, °C	Loss of mass by a sample in calcination, %	Qualitative composition of gases and vapors released in calcination
330	7.6	NH_3
370	2.3	H_2O vapor
580	12.5	NH_3 и SO_3

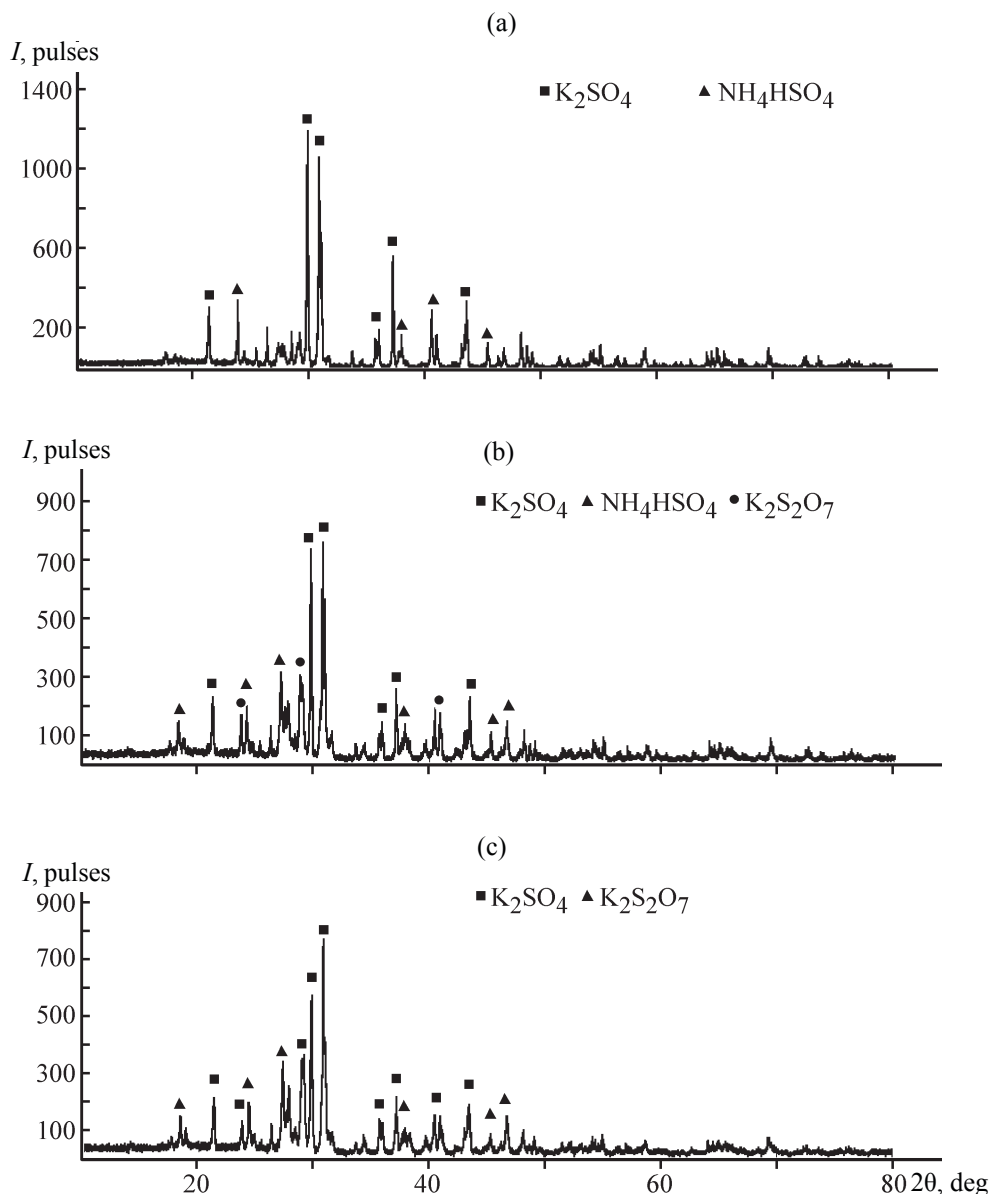
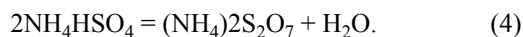


Fig. 3. X-ray diffraction pattern of the product obtained upon calcination of double potassium-ammonium sulfate at (a) 330, (b) 370, and (c) 580°C.

Therefore, its decomposition at 370°C is impossible. According to published data [4], ammonium hydrosulfate is recrystallized at 350–420°C by the reaction



Potassium pyrosulfate present in the product is formed as a result of the exchange reaction between ammonium pyrosulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_7]$ and potassium sulfate:

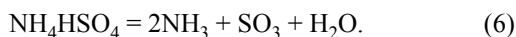


Ammonium sulfate formed by reaction (5) decomposes by reaction (3). Based on the thermogram in Fig. 2, we can conclude that the processes in which ammonium sulfate decomposes and ammonium hydrosulfate recrystallizes occur simultaneously in the temperature range 330–370°C. The presence of ammonium hydrosulfate in the product shows that its recrystallization is not complete.

An X-ray phase analysis of the product obtained in calcination of double potassium-ammonium sulfate at 580°C (Fig. 3c) demonstrated that the main phases

contained in the product are potassium sulfate (K_2SO_4) and pyrosulfate ($K_2S_2O_7$).

The absence of ammonium hydrosulfate in the product formed upon calcination in the furnace indicates that this compound completely decomposes at temperatures higher than $500^\circ C$ by the reaction [5]:



In the process, ammonia (NH_3) and sulfur trioxide (SO_3) are released into the gas phase. The pink coloration of the indicator in absorption of the gas evolving from the furnace in calcination of double potassium-ammonium sulfate at $580^\circ C$ is indicative of the acid nature of the evolving gas. When the released gases are absorbed by water in solution, there mutual neutralization occurs. Because the mass of sulfur trioxide released by reaction (6) exceeds the mass of ammonia, the medium in the absorbing solution remains acid.

CONCLUSIONS

(1) A study of the process in which potassium chloride is converted by sulfuric acid, with the subsequent neutralization with an ammonia solution, yielded double potassium-ammonium sulfate containing 97.2% main substance.

(2) A study of characteristics of double potassium-ammonium sulfate demonstrated that this compound is unstable against the action of high temperatures. The

melting point of double potassium-ammonium sulfate is $229.4^\circ C$. At $332.1^\circ C$, it decomposes to give potassium sulfate (K_2SO_4), ammonium hydrosulfate (NH_4HSO_4), and ammonia (NH_3). This process occurs with absorption of heat.

(3) At $369.6^\circ C$, the resulting ammonium hydrosulfate is recrystallized into the pyrosulfate, which enters into the exchange reaction with potassium sulfate to give potassium pyrosulfate ($K_2S_2O_7$), accompanied by the release of heat. The remaining ammonium hydrosulfate decomposes at $580.1^\circ C$ into sulfur trioxide, ammonia, and water. The decomposition reaction occurs with an endothermic effect.

(4) The thermal decomposition of double potassium-ammonium sulfate at temperatures above $500^\circ C$ yields potassium sulfate with admixture of potassium pyrosulfate.

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