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THERMODYNAMIC-KINETIC RESEARCH AND MATHEMATICAL PLANNING ON THE OBTAINING OF PHOSPHORUS-CONTAINING COMPONENTS BASED ON COTTREL DUST FROM PHOSPHORUS PRODUCTION WASTE

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ABSTRACT

The research work is designed to develop a technology for the disposal of phosphorus-containing waste through their complex processing to solve regional environmental problems. In this development, thermodynamic and kinetic patterns are determined and optimal process parameters are established using the method of mathematical planning of experiments.

Keywords: Cottrel Dust, Calcium Monophosphate, Technogenic Waste, Sulfuric Acid, Phosphorus-Containing Fertilizers.

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INTRODUCTION

At the present stage of the development of science and technology, one of the most important problems is the processing of natural and man-made waste. In recent years, the waste of raw materials and industrial products accumulated at factories and mines has created serious environmental problems in the regions. Therefore, their processing in order to obtain valuable products is an urgent task. Accumulated waste is considered complex and time-consuming work in terms of chemical and granulometric composition, as well as processing based on modern technologies.[1] Currently, as a result of the reduction of electric melting of phosphorous raw materials in phosphorus plant alone, about 150-160 kg of cottrel dust is formed per 1 ton of yellow phosphorus, which is discharged into evaporative pools in the form of a suspension –cottrel milk.[2] The resulting cottrel dust is considered as a secondary raw material, it can be used to obtain fertilizer since there is a proportion of phosphorus and other useful components in the composition of cottrel dust. At the same time, it becomes possible to obtain phosphorus-containing mineral fertilizers with a high content of useful components and trace elements.

EXPERIMENTAL

For the processing of cottrel dust under experimental conditions, test methods were selected a Jeol JSM-6490l V scanning electron microscope (SEM), a multiparameter portable cyber scanner (PCD 650 Eutech), an IR Fourier spectrometer (Zhimadzu IR Prestige-21) and an X-ray energy dispersive microanalyzer INCAEnergy (Oxford Instruments). Table-1 shows the material composition of cottrell dust.

Table-1: Material Composition of Cottrell Dust

Designation	Structure,%	Oxides	In terms of oxides,%
O	42,1	-	-
Na	0,84	Na_2O	1,13
Mg	0,91	MgO	1,51
Al	1,05	Al_2O_3	1,98

Si	7,31	SiO_2	15,6
P	13,4	P_2O_5	30,7
K	5,91	K_2O	7,12
Ca	6,35	CaO	8,89
Fe	0,58	Fe_2O_3	0,82
C	17,6	CO_2	-
Zn	0,55	ZnO	0,68
F	2,99	-	-

It follows from the analysis of Table-1 that the content of the main useful component in cottrell dust P_2O_5 is in the range of 30-31%, which is quite sufficient for their use as a phosphorus-containing component for the production of mineral fertilizers. The process of obtaining a phosphorus-containing component based on cottrel dust under laboratory conditions in accordance with GOST 21560-82. The process of obtaining a phosphorus-containing component is carried out by continuous stirring at a temperature of 60-90^{0}C for 60-120 minutes with solutions of 10% sulfuric acid. Due to an increase in the concentration of sulfuric acid used in the process of obtaining a phosphorus-containing component, the yield of the resulting product increases.[3-4] The chemistry of this process can be described as follows:

$$2Ca_5(PO_4)_3F + 7H_2SO_4 + 5H_2O = 3Ca(H_2PO_4)_2 \cdot H_2O + 7CaSO_4 \cdot 2H_2O + 2HF \qquad (1)$$

The material composition is defined with microscopy (JSM-6490lV, Jeol. Japan) on samples of a phosphorus-containing component - monocalcium phosphate, obtained on the basis of cottrel dust from the waste of the NovoDzhambul phosphorus plant. The results of the studies are shown in Table-2.

Table-2: Material Composition of Monocalcium Phosphate

Structure	Mg	Al	P	S	Ca	Na	Fe
Mass Fraction, %	0,04	0,25	11,45	0,08	8,05	-	0,6

It follows from Table-2 that at a 10% concentration of sulfuric acid and at a temperature of 90^{0}C, the phosphorus yield is 11.45%, such a phosphorus content is sufficient to use it as a phosphorus-containing component.

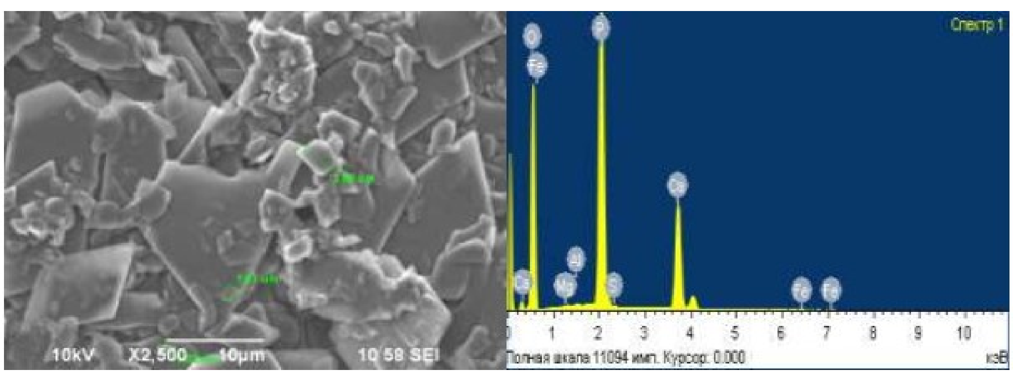

Fig.-1: Microscopic Image of Calcium Monophosphate

Based on the data in Fig.-1, the formation of a crystal structure in the microstructural image of the formed calcium monophosphate is described. It was found that the compound contains calcium, phosphorus, and a small amount of magnesium, iron, and aluminum.[5-7] The standard thermal effects of changes in the enthalpy, entropy, and Gibbs energy of the system at a temperature of 333-363K were determined using the complex program "HSC-6".[8] The data obtained are presented in Table-3 and Fig.-2. Based on the data in Table-3, it can be seen that when fluorapatite and sulfuric acid solution interact between the temperature of 333-363K, the Gibbs energy value changes from -292.28 to -282.14, and the

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course of the chemical reaction is explained by the negative Gibbs energy value. The change in the thermodynamic parameters of a chemical reaction is shown in the Fig.-2.

Table-3: Values of Thermodynamic Parameters in the Process of Dust Decomposition

Temperature, K	ΔH,kJ/ mol	ΔS, kJ / (mol* K)	ΔG, kJ / mol	Temperature, K	ΔH, kJ / mol	ΔS, kJ / (mol *K)	ΔG, kJ / mol
333	-399,29	-321,2	-292,28	353	-406,96	-343,57	-285,63
338	-401,25	-327,0	-290,66	358	-408,80	-348,75	-283,89
343	-403,19	-332,7	-289,01	363	-410,61	-353,77	-282,14
348	-405,09	-338,2	-287,33	-	-	-	-

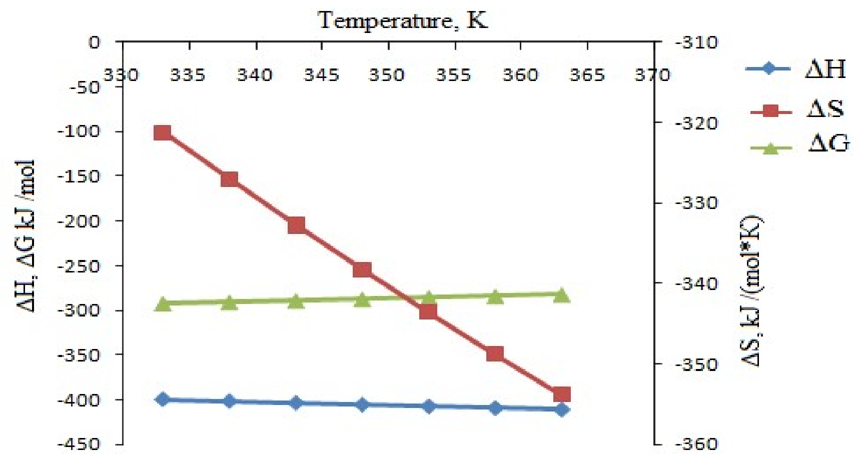

Fig.-2: Dependence of the Thermodynamic Parameters of the Reaction on the Temperature during the Decomposition of Dust

Figure-2 shows that due to an increase in temperature, the values of enthalpy and entropy in the system decrease, the Gibbs energy acquires a negative value and a chemical reaction occurs. Experimental data on the process of obtaining phosphorus compounds were processed according to the Pavlyuchenko equation (2), and the kinetic laws of the process were determined, with the calculation of the values of the "apparent" activation energy (3).

$$1-(1-\alpha)^{1/3} = K*\tau^{1/2} \quad (2)$$

$$K = A_0*e^{-E/RT} \quad (3)$$

where, E is the "apparent" activation energy, kJ /mol; R is a constant value of -8.314, and T is the process temperature. The degree of decomposition of cottrel dust depending on temperature and time during decomposition is shown in Fig.-3.

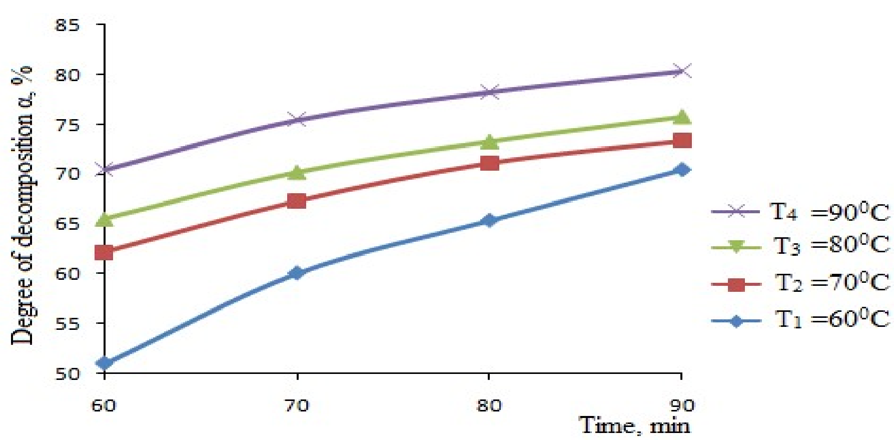

Fig.-3: Degree of Decomposition of Cottrel Dust Depending on Temperature and Time

Using the Pavlyuchenko equation[8-10] in determining the constant of the rate of the chemical reaction and the energy of "apparent" activation during the decomposition of cottrel dust with sulfuric acid solutions. Table -4 shows the results of processing experimental data.

Table-4: Results of Processing According To the Pavlyuchenko Equation

α	1-α	$(1-\alpha)^{1/3}$	$1-(1-\alpha)^{1/3}$	τ, min	$\sqrt{\tau}$
		T=333K			
0,510	0,490	0,788	0,222	60	7,745
0,601	0,399	0,736	0,264	80	8,944
0,654	0,346	0,702	0,298	100	10,00
0,702	0,298	0,667	0,333	120	10,95
		T=343K			
0,622	0,378	0,723	0,277	60	7,745
0,683	0,317	0,681	0,319	80	8,944
0,701	0,299	0,659	0,341	100	10,00
0,733	0,267	0,643	0,367	120	10,95
		T=353K			
0,655	0,345	0,701	0,299	60	7,745
0,702	0,298	0,667	0,333	80	8,944
0,723	0,277	0,645	0,355	100	10,00
0,748	0,252	0,621	0,379	120	10,95
		T=363K			
0,705	0,295	0,665	0,335	60	7,745
0,762	0,238	0,619	0,381	80	8,944
0,783	0,217	0,600	0,400	100	10,00
0,804	0,196	0,580	0,420	120	10,95

Figure-4 shows a graph of the dependence $1-(1-\alpha)^{1/3}$ от $\sqrt{\tau}$.

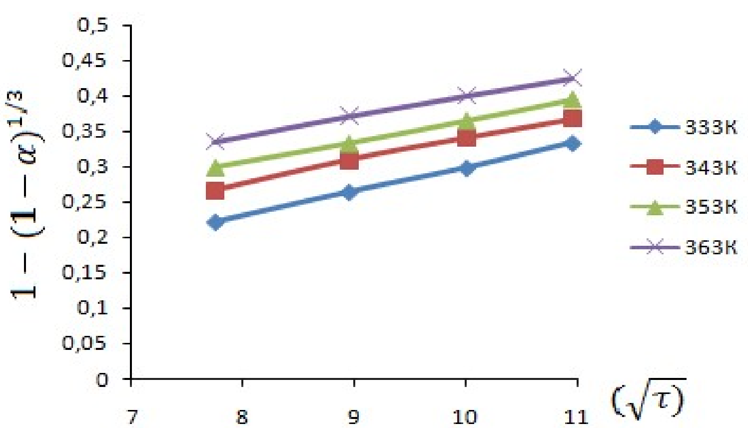

Fig.-4: Dependencies between $1-(1-\alpha)^{1/3}$ и $\sqrt{\tau}$

Table-5: The Relationship between the Value of the Velocity Constant and the Inverse Temperature

Constant speeds	Numerical value K	*lnK*	Temperature, K	*1/T*
$tg_{\varphi 1} = K_1$	0,0295	-1,530	333	0,0030
$tg_{\varphi 2} = K_2$	0,0355	-1,449	343	0,0029
$tg_{\varphi 3} = K_3$	0,0365	-1,436	353	0,0028
$tg_{\varphi 4} = K_4$	0,0401	-1,396	363	0,0027

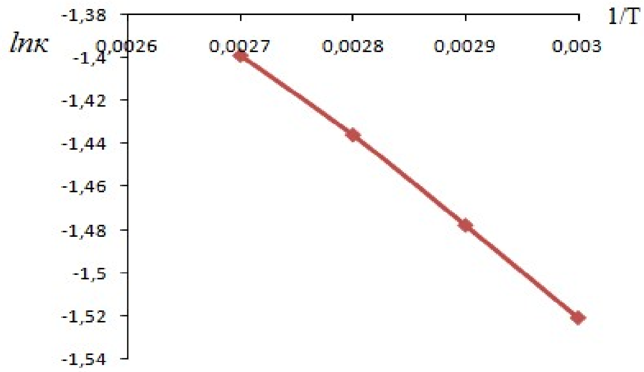

Fig.-5: Dependencies between *lnк=f(1/T)*

Methods of mathematical processing are considered in order to determine the reliability and reliability of the results of experimental work carried out in laboratory conditions. The equation of recording the degree of decomposition of cottrell dust based on a linear mathematical function is shown:

$$Z = 16,7213+0,4602*x+0,2009y \qquad (4)$$

The experimental data processed using the mathematical function of the decomposition process of cottrel dust are presented in Table-6.

Table-6: Dependence of the Degree of Decomposition of Cottrel Dust on Temperature Changes Over Time

Temperature,ºC	Time, min	Degree of decomposition of cottrel dust, α	Temperature, ºC	Time, min	Degree of decomposition of cottrel dust α
60	60	51,0	80	60	65,5
60	80	60,1	80	80	70,2
60	100	65,4	80	100	72,3
60	120	70,5	80	120	74,8
70	60	62,2	90	60	70,5
70	80	68,3	90	80	76,2
70	100	70,1	90	100	78,3
70	120	73,3	90	120	80,4

From the data in Table-6, it can be seen that with increasing temperature and time, the degree of decomposition of dust increases in the process. A mathematically processed version of the degree of decomposition of cottrel dust in a solution of sulfuric acid is shown in Fig.-6.

Based on the data in Fig.-6, an increase in the degree of decomposition under the influence of time and temperature during the decomposition of cottrel dust is characterized by a change in the square appearance of the plane from green to saturated red.

RESULTS AND DISCUSSION

During the research, it was determined that the degree of decomposition of cottrel dust is -80.4% with a solution of sulfuric acid concentration of 10% and a temperature of 90^0C. The total proportion of P_2O_5 oxide is within the phosphorus range of 24-25%, which is quite enough for their use as a phosphorus-containing component for the production of mineral fertilizers. Thermodynamic regularities of the process of decomposition of cottrel dust with a solution of sulfuric acid have been studied. The parameters of the value in the system of enthalpy, entropy, and Gibbs energy are determined using equations and the Outokumpu HSC-6 software package. The values of the "apparent" activation energy of the decomposition process of cottrel dust with a solution of sulfuric acid are determined. The value of the "apparent" energy of the activation of a chemical reaction is equal to Eq.= 5.94 kJ/mol. Based on the data obtained, it can be concluded that the chemical reaction of decomposition of cottrel dust with a solution of sulfuric acid proceeds in the diffusion region.[11]

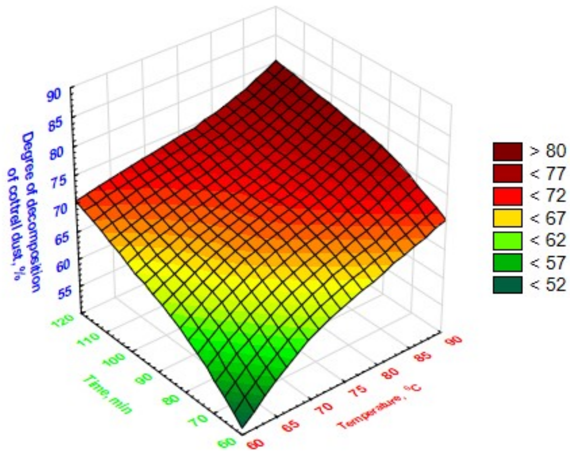

Fig.-6: Dependence of the Degree of Decomposition of Cottrel Dust on Temperature over Time

CONCLUSION

Technology has been developed to produce phosphorus-containing monocalcium phosphate based on cottrel dust from the waste of the Novo-Dzhambul phosphorus plant using sulfuric acid solutions. The research work is designed to develop a technology for the disposal of phosphorus-containing waste through their complex processing to solve regional environmental problems. The kinetic regularities of the process of obtaining phosphorus-containing monocalcium phosphate obtained on the basis of cottrel dust from the waste of the Novo-Dzhambul phosphorus plant have been studied. The features of the material composition of cottrel dust and the resulting phosphorus-containing monocalcium phosphate have been studied. The optimal technological parameters of this process and methods of mathematical planning of experimental work are established.

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