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Obtaining Fertilizer Products from Phosphorus and Sulfur Containing Secondary Feedstock.

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ABSTRACT

The possibility of obtaining fertilizing products from waste of phosphoric and oil and gas industry in a mixture with phosphorite under mechano-chemical activation and drying conditions is given in this paper. The fertilizer with a content of total P_2O_5 at the level of simple superphosphate (17-25%), which are characterized by high content of water-soluble phosphate forms were obtained by activation method in the presence of diluted H_2SO_4, H_3PO_4, HNO_3.

Keywords: liquid phase of cotrel “milk” (CM), oil sulphur, phosphorite of Karatau (PhK), mineral acids (MA), activation, drying, fertilizer.

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INTRODUCTION

In recent years the requirements of agro-chemists are directed to obtain fertilizers, which structure includes nourishing components such as phosphorus, potassium and sulphur. Phosphorites are traditional raw material to produce phosphorus fertilizers. Currently, the sulphur generated by the treatments of hydrocarbons and which can be used as an activating additive to phosphorite when its processing to phosphorus fertilizer, has an important place in the overall balance of substances that pollute the environment. The other large-tonnage phosphorus production waste – liquid phase of phosphorus sludge (cotrel "milk") can be used as a source of raw materials to obtain complicated phosphorus fertilizers, which include, along with phosphorus and sulphur also potassium. The method of mechanical activation is the effective method of joint processing of phosphorite with waste of phosphorus and oil and gas production. The essence of this method lies in the processing of phosphorite in the mix with the oil sulfur, liquid phase of poor sludge and diluted mineral acids in mills with high kinetic energy of milling bodies. This creates a high mechanical stresses in the material and is accompanied by phase transitions, transformations apatite structure, the component of phosphate ore, and digestible soluble forms. Diluted mineral acids can be used to deepen activation process [1, 2]. Mechanical activation of phosphorites with the aforementioned additives leads to an increase in the content of digestible P_2O_5 and allows receiving phosphorus, sulphur and potassium-containing high-quality fertilizer at the lowest cost, which are effective fertilizers when using them in agriculture, and also solves the problem of utilization of phosphorus, sulfur-containing secondary raw materials.

EXPERIMENTAL

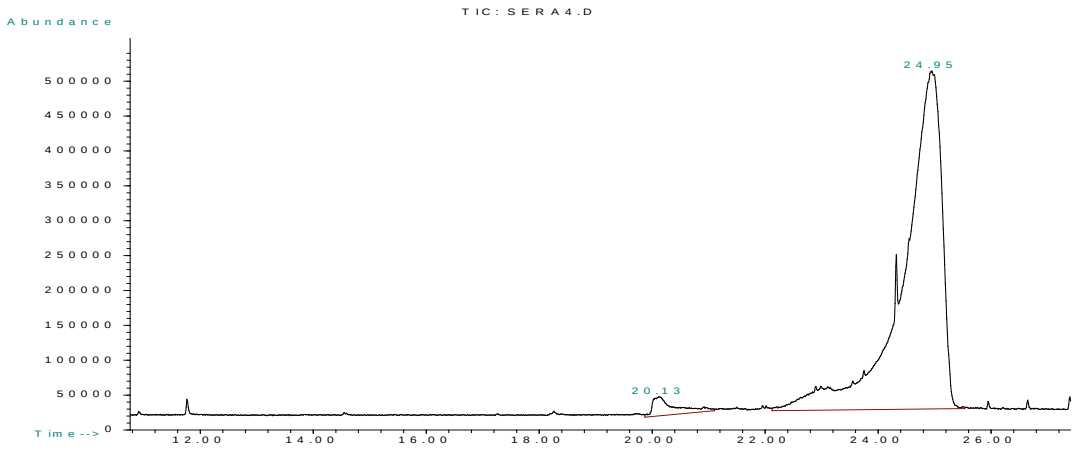
Materials and Methods

- Phosphorite of Karatau field (Republic of Kazakhstan) with a next content, mass %: P_2O – 24.8 $_5$; CaO – 37.5; MgO – 1.2; Fe_2O_3 – 1.2; Al_2O_3 – 1.3; CO_2 – 4.0; F – 2.3; LOI – 6.8; insoluble residue – 20.8.
- Liquid phase of phosphorus sludge, mass %: 3.2 - P_2O_5; 5.5 - K_2O; 0.03 - CaO; 0.01 – MgO; 0.6 - Si; 0.6 - Fe_2O_3; 1.5 - Zn.
- Sulphur - product of desulfurization of oil and gas deposits of Zhanazhol (Repoblic of Kazakhstan). According microelement analysis, sulphur contains total amount of organic impurities in mass %: C – 11.3; H – 2.0; N – 0.78; O_2 – 6.2. As is evident, the Zhanazhol sulfur includes organic impurities.

RESULTS AND DISCUSSION

The chromatogram of methylene chloride extract, which is the product of desulfurization of Zhanazhol oil in methylene chloride showed the presence of elemental sulfur of various shapes (figure 1). Intensive peak at 24.95 minutes referred to a modification of sulfur S_8. The shape of this peak, which has sloping wing to the side of less retention time, probably due to the presence of modified sulfur with more low molecular form. Relatively small peak at 20.13 minutes attributed to sulfur in the form of S_6.

Figure 1: Mass chromatogram of methylene chloride extract of sulphure without of treatment. τ – retention time 24.88 minutes



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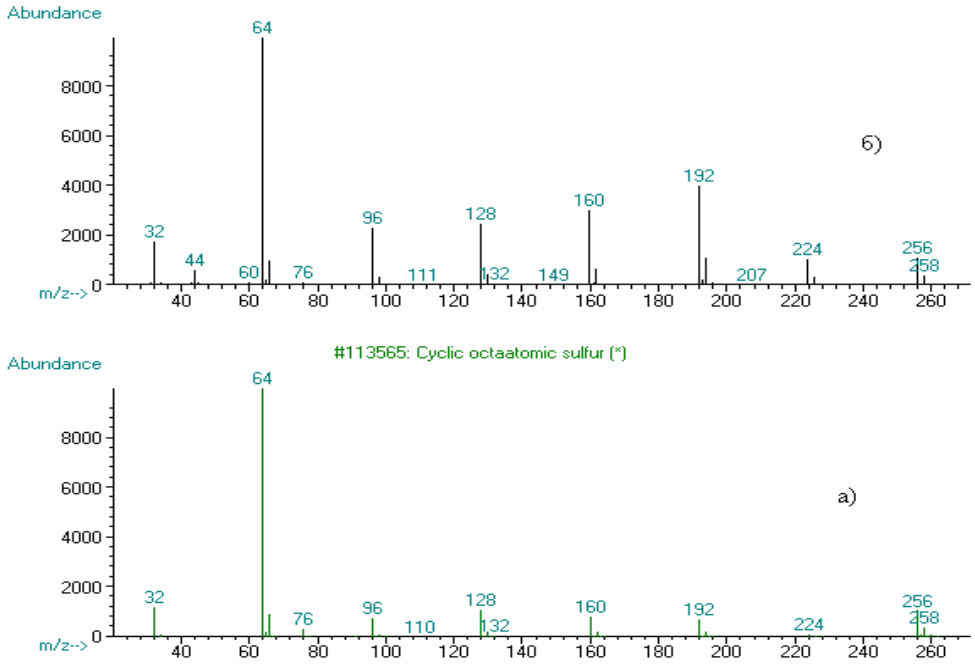
On the mass spectrum of sulphur (figure 2 b) the difference between the main peaks is 32 cu, which corresponds to the molecular weight of the sulphur. Comparison of the mass spectra of the oil sulphur with elemental sulfur (figure 2) confirms the presence of low molecular weight forms of S_2, S_3, S_4, S_5 with a predominance of S_2- forms of sulfur. Correlating the intensities of the peaks established that the content of S_2-forms is 40-42% of the total weight of the sulfur.

It should be noted that the sulfur is particularly dissolved when its extraction and at subsequent analysis it creates difficulties by closing hydrocarbon peaks in the chromatogram (figure 1 and 2). That is why there are methods of removing sulfur from the extracts. There is used sulfur removing method by using powder of metal copper. In this case, the sulfur is bound in insoluble copper sulphide and does not remain in solution even in trace amounts.

Sulfur analysis on hydrocarbon content was performed not only by gas chromatography-mass spectrometry, but also by using of IR - spectroscopy. In this case, the sample was extracted with carbon tetrachloride, and the spectrum was recorded in the area (3000-2700) cm^{-1}. This solvent does not absorb in this region, whereas any organic compound having a C-H bond strongly absorbs in this area. Analysis conducted by this method showed that the total content of hydrocarbons in the sample was 15 mg / kg. It should be recognized that as a low concentration, as comparison, the MPC for soils in the Netherlands is 800 mg / kg (in Kazakhstan MPC of oil in the soil is not installed).

Gas chromatography-mass spectrometry of methylene cloride extract showed presence of hydrocarbonse from C15 to C27 (figure 3). 29 substances were identified in total. These compounds have low volatility and do not represent an immediate threat to air basin. N-alkanes were dominated in the sample, their share was about 60% in the total mass (Table 1). In a small number attended branched alkanes. Aromatic compound were not found. Two peaks - octadecane (retention time 24.20 min.) and trikozan (retention time 26-29 min.) were observed in the chromatogram (figure 3). This distribution is often indicates about mix of light and heavy crude oils. The large amount of n-alkanes in the sample indicates that the storage time is small because n-alkanes primarily exposed to biodegradation and their relative content decreases.



a – sulfur, chemically pure; b – Zhanazhol sulfur

Figure 2: Mass spectra of Zhanazhol sulfur extract with signal of retention time 24.88 minutes in comparison with mass spectra of sulfur from NIST library

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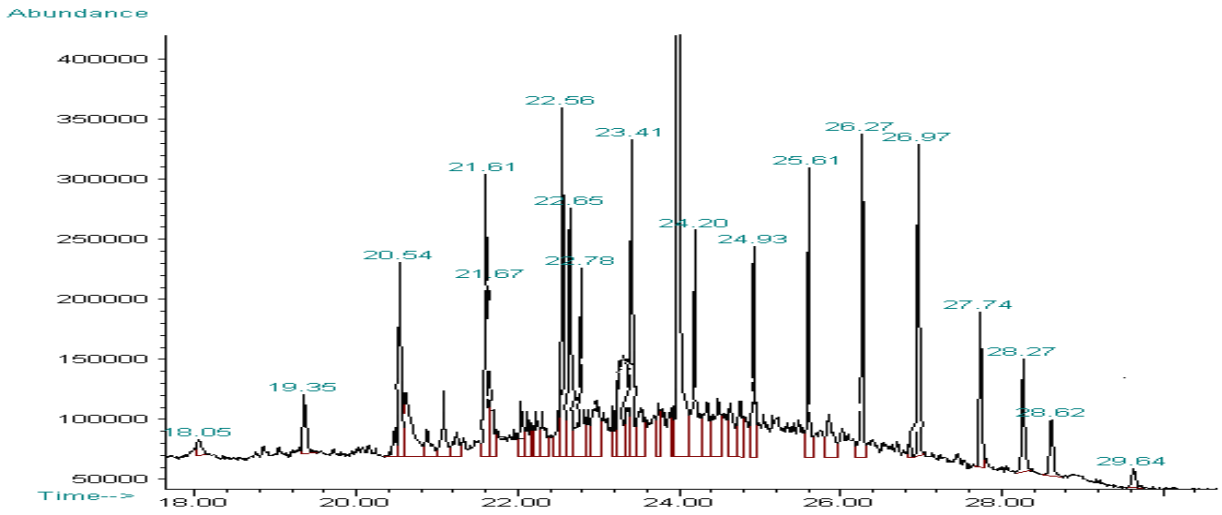

Figure 3: Mass chromatogram of methylene extract of technical sulfur of oil field

Most of the organic compounds, which are present in Zhanazhol sulfur content, are components of oil, were introduced into invariable kind during its desulfurization.

Table 1: The composition of the organic part of the technical sulfur of Zhanazhol gas processing plant

№	Retention time	Name of compound	% in organic	C, mg/kg
1	18,04	Tridecane, 2,5-dimethyl-	0,6000	0,09
2	19,35	Pentadecane	1,5333	0,23
3	20,48	1-Hexadecene	0,7333	0,11
4	20,55	Hexadecane	4,2000	0,63
5	21,6	Heptadecane	4,6667	0,7
6	21,67	Tetradecane, 2,6,10,14-tetramethyl-	3,6000	0,54
7	22,04	Hexadecane, 3,4-dimethyl-	1,8000	0,27
8	22,13	Hexadecane, 2,4-dimethyl-	1,1333	0,17
9	22,23	Heptadecane, 4-methyl-	1,4667	0,22
10	22,3	Heptadecane, 3-methyl-	1,5333	0,23
11	22,55	Octadecane	5,8000	0,87
12	22,65	Heptadecane, 2,6- dimethyl -	5,2667	0,79
13	22,87	Heptadecane, 2,5- dimethyl -	1,2667	0,19
14	23,19	Cyclohexane, dodecyl	1,0667	0,16
15	23,36	Heptadecane, 2,6- dimethyl -	1,8667	0,28
16	23,42	Nonadecane	5,4000	0,81
17	23,74	Octadecane, 2,8- dimethyl -	1,4000	0,21
18	23,92	Octadecane, 2,9- dimethyl -	1,1333	0,17
19	24,2	Eicosane	6,2667	0,94
20	24,49	Heptadecane, 2,6,9,14-tetramethyl	3,4000	0,51
21	24,76	Heptadecane,2,6,10,14-tetramethyl	2,2667	0,34
22	24,93	Henacosane (Хенэйкозан)	4,3333	0,65
23	25,61	Docosane	4,8667	0,73
24	25,86	Docosane, 2-methyl-	2,1333	0,32
25	26,28	Tricosane	5,2667	0,79
26	26,98	Tetracosane	4,9333	0,74
27	27,74	Pentacosane	2,8000	0,42
28	28,61	Hexacosane	1,5333	0,23
29	29,63	Heptacosane	0,6000	0,09

Analysis of aqueous extract of sulfur showed that polar hydrocarbons are practically absent in the sample. This indicates that, at first, in the process of desulfurization the oxidation of condensate components significantly not occures, and secondly, during storage hydrocarbons have not been subject of biodegradation.

Thus, it was found that in the product of desulfurization of Zhanazhol oil and gas raw material the sulfur of S_8-forms presented in a mixture of low molecular weight S_2, S_3, S_4-forms, most of which falls on the S_2-form, and organic impurities are mainly in the form of saturated hydrocarbons, n-alkanes with cyclic hydrocarbon admixtures.

It is known that impurities have a significant role on structure and properties of sulfur [3-5]. That Is Why it can be expected that the sulfur –the waste of petroleum refining, show chemical reactivity in mechanical-chemical methods of obtaining hard-phosphate fertilizers.

Due to the above stated there is investigated the process of obtaining fertilizing products from Karatau phosphorite (FC), sulfur oil, liquid phase cotrel "milk" (CM), with the addition of mineral acids (MC) in terms of activation and drying. 5% solutions of sulfuric, phosphoric and nitric acids were used as the mineral acid. The feedstock (liquid phase of cotrel "milk", oil sulfur, Karatau phosphorite) were mixed in a predetermined ratio to obtain a fertilizing product with total P_2O_5 content at superphosphate level, and small amount of acid (0.3-1 wt. H.) were added. Then the mixture was subjected to mechanical activation and further dried at 110-115^oC to constant weight. The total P_2O_5 and water-, citrate-, lemon-, salt-soluble forms of P_2O_5 characterizing their effectiveness as fertilizers were determined in the finished products [6].

As shown in table 2, addition of dilute mineral acid in the mixture of liquid phase of CM, S_{oil} and PhK increases the total content of P_2O_5. It means, there is deepening the process of decomposition in activation and drying conditions. The fertilizers with total 24.26-25.9% content of P_2O_5 (on level of simple superphosphate from apatite concentrate) were obtained at a ratio S:CM liquid phase:PhK:MA = 5:100:10:0.3. Regardless of the nature of the acid reagent the most of P_2O_5 (83.8-94.9 rel.%) is in the salt-soluble form and 30.1-33.9 rel.% in lemon-digestible form. The nature of acid has a significant impact on the content of salt-soluble and slightly less on the content of lemon-soluble P_2O_5. Thus, in product produced with the addition of H_2SO_4, P_2O_5 content, which is digestible in citric acid is 34.1 rel.%, with H_3PO_4 – 30.1 rel.%, with HNO_3 – 33.9 rel.%, and in 0.4% HCl respectively 83.8 rel.%, 87.8 rel.% and 94.9 rel.%. Nitric acid is more active in relation to used raw material source.

Table 2: Properties of fertilizing products, which are obtained under the ratio S:CM liquid phase:PhK:MA = 5:100:10:0.3

The ratio of reagents	P_2O_5 content, %				
	total	Water-soluble	Soluble in Trilon B	Lemon-soluble	Soluble in 0.4% HCl
$S_{oil.}$:liq.ph.CM:PhK=10:5:100	23.88	abs	abs	7.74	20.77
$S_{oil.}$:liq.ph.CM:PhK : H_2SO_4= 10:5:100:0.3	24.26	abs	abs	8.28	20.32
$S_{oil.}$:liq.ph.CM:PhK:H_3PO_4= 10:5:100:0.3	25.90	abs	abs	7.80	22.73
$S_{oil.}$:liq.ph.CM:PhK:HNO_3= 10:5:100:0.3	24.45	abs	abs	8.29	23.21

Further experiments were carried out to optimize the process of producing fertilizer from an oil sulfur, liquid phase of KM, Karatau Phosphorite with addition of dilute mineral acids by mechanical-chemical activation of activated mixture, followed by drying (see Table 3).

As can be seen from Table 3 in the produced fertilizers is no water- and citrate-digestible P_2O_5. Therefore, research has focused on producing more universal fertilizing products in which would be water-and citrate- soluble phosphate forms.

The results of table 3 shows, that increasing the norms of liquid phase of cotrel “milk” in 20 times and mineral acids in 3.3 times (experiments #5-8) in relation to previous experiments (experiments 1-4) rises the content of total P_2O_5 up to level of enriched superphosphate (30-31%) due to its additional injection of liquid phase of CM and deeper decomposition of raw phosphate with acid supplement. However, there is also no water-soluble P_2O_5 in produced fertilizer products, but it appears citrate-digestible (soluble in Trilon-B). Its

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content does not depend on the nature of the acid reactant and varies between 11.8-12.8%. Content of lemon- and salt-soluble phosphate forms decreases.

Table 3: Conditions of producing and properties of fertilizing products at different ratios S_{oil}:liq.ph.CM:PhK:MA

#	The ratio of reagents	P_2O_5 content, %					assimilable P_2O_5, rel. %			
		total	Water-soluble	Trilon B sol.	Citric acid sol.	Soluble in 0.4% HCl	in H_2O	In Trilon B	in 2% citric acid	in 0.4% HCl
1	S_{oil}:liq.ph.CM:PhK =10:5:100	23.88	abs	abs	7.74	20.77	abs	abs	32.4	87.0
2	S_{oil}:liq.ph.CM:PhK : H_2SO_4 =10:5:100:0.3	24.26	abs	abs	8.28	20.32	abs	abs	34.1	83.8
3	S_{oil}:liq.ph.CM:PhK : H_3PO_4=10:5:100:0.3	25.90	abs	abs	7.80	22.73	abs	abs	30.1	87.8
4	S_{oil}:liq.ph.CM:PhK : HNO_3=10:5:100:0.3	24.45	abs	abs	8.29	23.21	abs	abs	33.9	94.9
5	S_{oil}:liq.ph.CM:PhK =10:100:100	30.89	abs	3.66	6.23	19.72	abs	11.9	20.2	63.8
6	S_{oil}:liq.ph.CM:PhK : H_2SO_4 =10:100:100:1	25.75	abs	3.30	6.43	19.90	abs	12.8	25.0	77.3
7	S_{oil}:liq.ph.CM:PhK : H_3PO_4= 10:100:100:1	30.89	abs	3.66	6.48	18.86	abs	11.8	21.0	61.1
8	S_{oil}:liq.ph.CM:PhK : HNO_3= 10:100:100:1	30.00	abs	3.65	6.48	27.30	abs	12.2	21.6	91.0
9	S_{oil}:liq.ph.CM:PhK = 10:100:200	14.79	abs	2.46	3.36	12.69	abs	16.6	22.7	85.8
10	S_{oil}:liq.ph.CM:PhK : H_2SO_4 =10:100:200:5	14.15	abs	2.46	4.64	13.43	abs	17.4	32.8	94.9
11	S_{oil}:liq.ph.CM:PhK : H_3PO_4= 10:100:200:5	14.36	abs	2.46	4.22	13.87	abs	17.1	29.4	96.6
12	S_{oil}:liq.ph.CM:PhK : HNO_3= 10:100:200:5	16.42	abs	2.46	3.68	14.05	abs	15.0	22.4	85.6
13	S_{oil}:liq.ph.CM:PhK =10:20:100	16.03	5.29	7.44	11.92	16.00	33.0	46.5	74. 5	99.8
14	S_{oil}:liq.ph.CM:PhK : H_2SO_4=10:20:100:0.3	17.0	4.80	7.96	10.78	16.10	28.2	46.8	63.4	94.7
15	S_{oil}:liq.ph.CM:PhK : H_3PO_4=10:20:100:0.3	18.5	5.29	6.97	9.56	16.50	28.6	37.7	51.7	89.2
16	S_{oil}:liq.ph.CM:PhK HNO_3=10:20:100:0.3	17.0	4.29	5.80	9.00	16.89	25.2	25.2	52.9	99.4
17	S_{oil}:liq.ph.CM:PhK =10:300:10	23.54	15.5	20.85	18.65	22.27	65.9	88.6	79.2	94.6
18	S_{oil}:liq.ph.CM:PhK : H_2SO_4 =10:300:10:1	24.40	17.0	23.66	18.65	20.37	69.7	97.0	76.4	83.5
19	S_{oil}:liq.ph.CM:PhK : H_3PO_4= 10:300:10:1	23.52	16.3	20.32	22.26	21.75	69.3	86.4	96.1	92.5
20	S_{oil}:liq.ph.CM:PhK : HNO_3= 10:300:10:1	25.22	15.7	22.86	20.89	21.83	62.2	90.6	82.8	86.5

The raising of norms of Karatau phosphorite 2 times and the acid reagent 5 times (experiments 9-12) reduces the total P_2O_5 to 14.8-16.4% (to the level of simple superphosphate of Karatau phosphorite) in comparison with experiments 5-8 and also does not allow the fertilizer with water-soluble form of P_2O_5. In this case, in fertilizers increased the content of citrate-digestible P_2O_5 in 1.3-1.45 times and salt-soluble P_2O_5 in 1.1-1.5 times. It should be noted that the content of assimilable phosphate forms practically does not depend on the nature of the acid reactant.

Reducing the flow rate of liquid phase of CM in 5 times and of the mineral acid in 16.7 times (experiments #13-16) in comparison with experiments #9-12 retains the total P_2O_5 content substantially at the previous level, but allows to obtain a fertilizer with P_2O_5, digestible in H_2O ($K_{deg\ H2O}$ = 25.2-33.0 rel.%). This

significantly increases the content of citrate- and citric-digestible P_2O_5, respectively (1.7-2.8) times and (2-3.3) times. It is possible that using less liquid phase of cotrel "milk" in the process of decomposition of phosphorite increases the share of the impact of oil sulfur.

As seen from experiments #17-20 phosphorite of Karatau load reduction to 10 times with a simultaneous increase in the norm liquid phase of CM in 3 times and acid in 3.3 times as compared to experiments #13-16 total P_2O_5 content increases to 23.5 -25.2%. The content of water-soluble P_2O_5 increases (2-2.5) times ($K_{deg\ H2O}$ = 66-70 rel.%), digestible in Trilon B - in (2-3.5) times ($K_{deg\ in}$ Trilon B = 89-97 rel.%), and digestible in 2% citric acid in (1.1-1.6) times ($K_{deg\ \%\ lim.\ acid}$ = 76-83%).

Thus, the fertilizers obtained from the liquid phase of the mixture of cotrel "milk", oil sulfur, Karatau phosphorite in the presence of dilute H_2SO_4, H_3PO_4, HNO_3 by activating, with the content of 17-18% and total 24.4-25% P_2O_5 at level of simple superphosphate, respectively derived from phosphorite of Karatau and apatite (experiments #13-20), but in contrast to them are characterized by a high content of water-degistible forms of P_2O_5.

Involvement in the joint processing of phosphorite and secondary raw materials (sulfur and phosphorus sludge liquid phase) with mechanical-chemical method will reduce the acid consumption per unit of finished product, which is an actual problem of phosphate fertilizer industry. In addition, utilization of oil sulfur and phosphorus sludge liquid phase in the bulk manufacture of mineral fertilizers simultaneously solves the acute environmental problems in the industrial regions.

REFERENCES

[1] YG Avakumov. Mechanical Methods of Activating of Chemical Processes, Novorossiisk: Nauka, 385, 1986.
[2] MV Chaikina, GN Kryukova. Structural Transformations Fluorapatite Indentation of Single Crystals and Activation in a Planetary Mill//ed. SO AN USSR, ser. Chem. Sc., 150-157, 1989.
[3] Physical-chemical properties of sulfur/obz.NIITEChIM.-M., 40, 1985.
[4] M Menkovski, VT Yavorski, Polymer sulfur//Technology of sulfur/Ed. I.V. Lebedyeva– M.: Chemistry, 328, 1985.
[5] Natural sulfur. Ed Doct of Chem Sci, Prof. MA Menkovski M, 150, 1972,
[6] GOST 20851.1-75-GOST 20851.4-75. Mineral fertilizers. Methods of analysis. M.: Gos.kom.Stand.USSR: ed. of standards, 58, 1975.