



The Results of Physico-Chemical and Microscopic Investigations of Phosphorus Sludge

U.B. NAZARBEEK^{*1}, U. BESTEREKOV¹, S.P. NAZARBEEKOVA² and A.A. BOLYSBEK¹

¹Department of Chemical technology of inorganic Substances,

²Department of Chemistry, M.Auezov South Kazakhstan State University,
South-Kazakhstan region, Republic of Kazakhstan.

*Corresponding author e-mail: unazarbek@mail.ru

<http://dx.doi.org/10.13005/ojc/310123>

(Received: November 30, 2014; Accepted: January 03, 2015)

ABSTRACT

The results of physico-chemical and microscopic investigations of phosphorus sludge are considered. It was established that phosphorus sludge does not meet regulatory requirements for mineral fertilizing on granulometric composition. On chemical composition, phosphorus sludge is close to original phosphate raw material of Karatau deposit, but it differs from latter by its less content of phosphate component and presence of constituents of charge mixture – quartzite and coke. The results of microscopic investigations show that phosphorus sludge structure contains mainly calcium silicates, diopside, and potassium aluminosilicates. The presence of latter ones allows that phosphorus sludge is a valuable secondary phosphate raw material, quite suitable for recycling of it into phosphorus, potassium containing complex mineral fertilizer.

Keywords: phosphorus sludge, microstructure, chemical analysis, granulometric composition, elemental composition, sieve analysis.

INTRODUCTION

At the present time, the dumps of the former Shymkent production organization (ShPO) “Phosphorus” in southern Kazakhstan in six sludge storages with a total area of over 30 hectares contains about 500,000 tons of phosphorus sludge. Recycling of it is important from both an environmental and economic points of view. Phosphorus sludge is formed due to the specificity of modern ore-thermal technology of extraction of

elemental phosphorus from phosphorite, which is chemically identical to raw material as phosphorite^{1,2,3,4}. However, it follows that phosphorus sludge differs from primary raw material by its composition, physico-chemical and microscopic properties and characterized by a number of individual properties, as phosphorus sludge is formed from a charge mixture consisting of phosphorite, coke and quartzite. In addition, a granulometric composition of phosphorus sludge will also significantly differ from the composition of

a charge mixture mass of phosphorus production. At this moment, practically all phosphorus sludge of ShPO "Phosphorus" has undergone a special vapor-heat treatment in LP "Kaynar" for the purpose of separation of free phosphorus from its composition, which is approximately composed over 90 thousand tons. Consequently, initial phosphorus sludge has undergone a number of changes, which affect on its characteristic indicators and properties⁵. In this regard, the study of granulometric composition, physical and chemical properties and peculiarities of sludge secondary phosphate raw materials are the actual problem.

MATERIALS AND METHODS

Samples of phosphorus sludge uniformly were collected from different levels of sludge tanks. Sieve analysis of samples was carried out according to the State Standard 21560.-82 "Mineral fertilizers. Method for determination of granulometric composition" using a vibrating sieve rumble of "Analysette 3" of PRO model.

Chemical analysis of phosphorus sludge was carried out in compliance with the regulatory requirements of the State Standards: 3760-79, 9264-79, 9336-75, 3765-78, 3773-72, 4109-79, 6709-72, 4198-75, 4461-77, 3652-69, 4209-77, 5850-72, 4234-77, 4204-77, 3118-77, 10484-78, 4212-78, 25336-82, 1770-74, 20292-74, 4144-79, 18300-72, 24363-80, 10652-73, 10398-76, 12083-78, 4478-78, 199-78, 3117-78, 61-75, 25794-83 and others.

Phosphorus sludge was subjected to microstructural analysis using a scanning electron microscope JEOL, brand JSM6490 LV.

Microstructure and element-weight composition of phosphorus sludge samples were studied at 40 and 500 times magnification.

RESULTS AND DISCUSSION

Figure 1 presents the results of sieve analysis of the investigated phosphorus sludge of LP "Kaynar". The data from Diagram 1 show that 1/3 part of the phosphorus sludge is equal to the share of fine fraction with a particle size of 0,100-0,315

mm. In total weight of phosphorus sludge about 5% is a large fraction with a size of greater than 1.4 mm. The share of dust particles of phosphorus sludge is about 20%. Basic mass of phosphorus sludge constitutes fractions with dimensions: 1.0 -1.4 mm; 0,71-1,0 mm; 0,50-0,71 mm; 0,315-0,500 mm. As it's seen from the data of diagram 1, mass fraction of these fractions is approximately the same, and the average is 12%.

It follows that the phosphorus sludge by natural granulometric composition does not meet modern requirements for products of fertilizing purposes⁶. In developing the method and recycling technology of it into the fertilizer it is necessary consider these features and provide opportunities for a preliminary enlargement of particles of slurry mass or finish granulation of obtained desired product on the basis of phosphorus sludge.

Results of chemical analysis of phosphorus sludge samples are given in Tables 1,2. Phosphorus sludge samples were taken from all six sludge tanks with different markers in height. From which it is visible that the test samples as a whole on chemical composition is not significantly differed from each other and close to the original phosphate raw of Karatau deposit with inclusions composed of charge mixture mass - quartzite and coke. Comparative analysis of the data of Tables 1,2 with the known data about the chemical composition of phosphorites of Karatau⁷ shows that the noticeable reduction of concentrations of P_2O_5 , Na_2O , CaO , Al_2O_3 , F , and the substantial increase of K_2O , SiO_2 , MgO , C and Σ heavy metals contents are observed in the phosphorus sludge. It follows that the fertilizing value of phosphorus sludge by P_2O_5 lower than phosphorite and phosphorus sludge is advantageously differed by the content of K_2O from the latter one. Moreover, practically three times increase of the content of silicon oxide, two times increase of the content of magnesium oxide and the appearance of free carbon, as well as exposure of noticeable presence of heavy metals in the phosphorus sludge causes the necessity to incorporate these features at the development of production technology of quality fertilizing product on the basis of phosphorus sludge.

Data of the Figure 2 follows that the general

Table 2: Chemical composition of phosphorus sludge by sludge tanks 4-6

Component	The content of components in samples, %																
	Sludge tank №4						Sludge tank №5						Sludge tank №6				
	sample 1	sample 2	sample 3	sample 4	sample 5	average by the sludge tank №4	sample 1	sample 2	sample 3	sample 4	sample 5	average by the sludge tank №5	sample 1	sample 2	sample 3	sample 4	sample 5
P ₂ O ₅ , total	16,75	15,62	12,62	22,50	15,60	16,62	16,50	16,70	17,25	17,50	18,30	17,25	11,25	9,25	15,0	1	
P ₂ O ₅ , water-soluble	3,74	3,55	2,41	6,60	3,28	3,93	2,50	1,81	1,40	1,90	3,40	2,20	1,45	1,37	2,62	1	
P ₂ O ₅ , sol. in citric acid	9,81	10,01	10,00	7,00	7,30	8,82	9,04	7,05	4,00	5,75	6,87	6,54	5,41	3,44	6,25	5	
K ₂ O	9,15	6,65	6,03	9,88	9,64	8,27	5,26	4,22	10,12	10,12	10,85	8,11	1,81	1,81	1,56	1	
Na ₂ O	1,28	0,22				0,75	0,12	0,88				0,50	0,02	0,02	0,76	0	
SiO ₂	48,10	47,2	59,84	50,56	50,79	51,30	47,66	43,44	48,04	45,32	42,04	45,30	55,02	70,60	33,65	3	
CaO	9,09	13,29	11,61	14,69	14,69	12,67	14,55	14,97	15,53	16,93	16,09	15,61	10,07	7,13	16,24	1	
MgO	1,81	2,16	3,58	4,03	4,02	3,12	0,99	3,78	4,48	4,92	5,80	3,10	1,39	2,39	4,0	7	
Al ₂ O ₃	1,53	0,38				0,95	0,76	0,77				0,76	0,77	1,13	2,20	1	
Fe ₂ O ₃	0,61	0,60				0,60	0,60	1,00				0,80	0,80	0,40	0,92	0	
F	0,06	0,06				0,06	0,10					0,10	0,15	0,24	0,51	0	
C	4,92	3,30				4,11	9,62	21,19				15,40	4,90	4,24	7,31	5	
S	0,29	0,33				0,31	0,42	0,37				0,39	0,97	0,26	0,39	0	
As															0,002	0	
Σ heavy met.															0,41	0	

Table 3: The elemental and weight compositions of phosphorus sludge in 40 and 500 times magnification (spectra 2-3)

Element	Weight composition, %	Weight composition, in terms of oxides, %	Sample enlarged 40 times		Sample enlarged 500 times (spectrum 2)		Sample enlarged 500 times (spectrum 3)	
			Element	Weight composition, %	Element	Weight composition, %	Element	Weight composition, in terms of oxides, %
O	42,65		O	27,55	O	30,76	O	0
F	11,76	11,76	F	3,75	F	22,74	F	22,74
Na	0,72	0,97056	Na	0,22	Na	0,57	Na	0,76836
Mg	1,59	2,63622	Mg	1,13	Mg	1,19	Mg	1,97302
Al	1,17	2,2113	Al	1	Al	1,21	Al	2,2869
Si	18,94	40,51266	Si	31,33	Si	13,99	Si	29,92461
P	6,26	14,34166	P	4,56	P	6,74	P	15,44134
S	0,57	0,57	S	0,73	S	0,23	S	0,23
Cl	0,09	0,09	K	7,06	K	2,38	K	2,8679
K	3,42	4,1211	Ca	22,66	Ca	19,5	Ca	27,2805
Ca	11,48	16,06052	In total	99,99	In total	100,01	Fe	1,001
Mn	0,2	0,28402					In total	104,5136
Fe	0,68	0,9724						
Zn	0,25	0,25						
Pb	0,17	0,18309						
In total	99,97	94,96						

structure of the analyzed sample is characterized by inclusions of large minerals of calcium silicates $2\text{CaO} \cdot \text{SiO}_2$ and small grains of wollostonite $\text{CaO} \cdot \text{SiO}_2$. It is also observed the presence of single minerals of $\text{CaO} \cdot \text{Al}_2\text{O}_3$, compounds of potassium aluminosilicates, calcium phosphate $3\text{CaO} \cdot \text{P}_2\text{O}_5$ and fluoride CaF_2 .

Figure 1 (spectrum 2) shows the part of an investigated sample of phosphorus sludge at 500 times magnification. The analyzed part clearly illustrates the presence of minerals $2\text{CaO} \cdot \text{SiO}_2$, $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot \text{SiO}_2$ and calcium phosphate and fluoride here. The presence of hydrated compounds of calcium phosphate in the studied sludge sample is characterized by film and unformulated structure of minerals.

In the spectrum 3 (Figure 2) is also given the part of the testing sludge sample, obtained at 500 times magnification. Basic mass of this structure is presented by minerals $2\text{CaO} \cdot \text{SiO}_2$. Here, the inclusions of metallosilicate and calcium aluminate are also presented. Between silicate and aluminate phases is given insignificant inclusions of ferrites of calcium ($\text{CaO} \cdot \text{Fe}_2\text{O}_3$), diopside ($\text{CaO} \cdot \text{MgO} \cdot 2\text{SiO}_2$) and calcium fluoride⁸. Calcium silicates and aluminates constitute 60-65% in total mass of microstructures of the samples.

The inclusion content of calcium ferrites and diopside do not exceed 13-15%. Weight content of calcium fluoride inclusions reaches up to 5% (Figure 2, Table. 3).

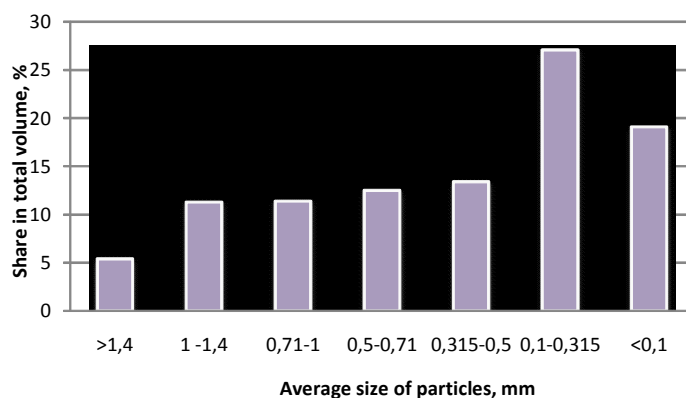


Fig. 1: Sieve analysis results of phosphorus sludge

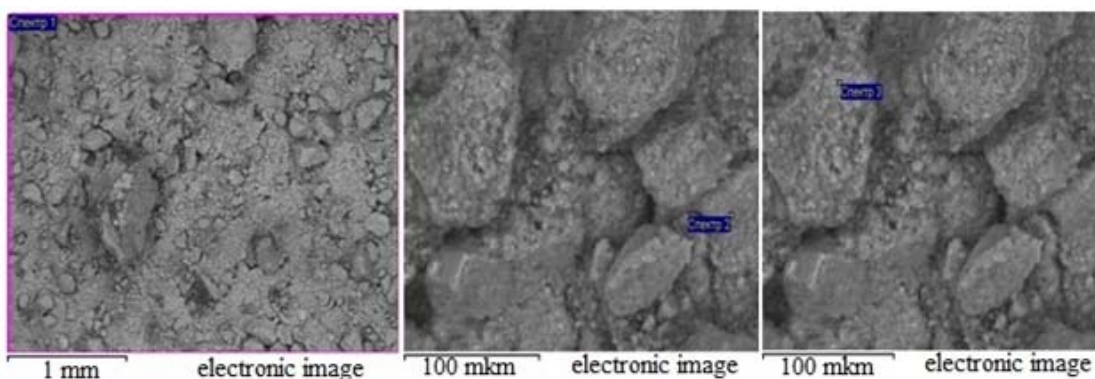


Fig. 2: Microstructure of the samples, enlarged 40 and 500 times (spectra 2 and 3)

Analysis of the microstructure of investigated samples of phosphorus sludge shows that their structure contains mainly calcium silicates, diopside and potassium aluminosilicates. By this

phosphorus sludge is enriched to a certain extent by alkali oxide - K_2O . Moreover in phosphorus sludge the ratio of $\text{SiO}_2 \setminus \text{CaO}$ is 2 that practically corresponds to the module of acidity of initial charge

mixture is 0.85. Consequently, in the presence of residual free phosphorus in phosphorus sludge is possible the formation of silicon pyrophosphate that contributes to an increase of the content of available phosphorus⁵.

Thus, the results of conducted studies suggest that phosphorus sludge is a valuable secondary phosphate raw material, quite suitable for recycling it into phosphorus, potassium, containing complex mineral fertilizer.

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