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Receiving Humic Plain Superphosphate on the Basis of the Private Phosphoric Meal of the Central Kyzylkum and the Oxidized Brown Coal of the Angren Field

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ABSTRACT. The structure of the samples of humic plain superphosphate received by decomposition of an ordinary phosphoric meal by sulfuric acid of 92% concentration in various norms (from 40 to 100% of a stoichiometryor formation of the monocalsiumphosphate) and additive sour superphosphate weight before ammonization and drying of the oxidized coal of the Angren field is studied by nitric acid at weight ratios phosphorene: coal (organic part of initial coal) =1:(0,05-1). It is shown that before ammonization and drying brings additions of the oxidized coal into the sour superphosphate mass of the oxidized coal to decrease as usual occurs when receiving plain superphosphate decomposition of phosphorene's sulfuric acid, the subsequent ammonization and drying, and to significant increase in relative contents the assailable of P_2O_5 forms. The optimum norm (60%) of sulfuric acid and weight phosphorene ratios to the oxidized coal is found (1:0,25), at which the fertilizer containing P_2O_{5gen} turns out 8,85%; P_2O_{5acq} on citric acid of 6,39%, i.e. $P_2O_{5acq.}$:P_2O_{5gen}. 72,20%; nitrogen 2,25%; organic matter 10,46%; humic acids of 4,71%, $CaO_{gen.}$ 29,06%, $CaO_{acq.}$ 4,21%, SO_{3gen}. 19,41%.

KEYWORDS: humic substances, humic acids, a phosphorus-humus, the oxidized coal.

I. INTRODUCTION

Organomineralfertilizers have fundamental long-term values of stabilization of receiving high and qualitative a harvest from crops. At applications the organomineralof fertilizers they resupplying nutrients in soils for plants at the same time serve sources of the humic substances providing preservation fertility of soils.

II. SIGNIFICANCE OF THE SYSTEM

In article receiving humic plain superphosphate on the basis of the private phosphoric meal central Kyzylkum and of the oxidized brown coal of the Angren field is considered. The study of literature survey is presented in section III, methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. LITERATURE SURVEY

In works it is in detail given [1-5] values and the mechanism of action the organomineral of fertilizers at applications in agricultural production. The humic substances which are a part of fertilizers promote the best assimilation by plants of basic elements of food. They the assimilable of phosphates prevents retro gradation, incorporates minerals, physiological and growth active substances, form friable structure, create favorable conditions for life of microorganisms, stimulate growth and development of plants. Organomineral fertilizers are capable to adsorb and hold nutritious elements, and their high ability also to moisture adsorption, prevents and excludes a possibility of

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washing away of batteries in the subsoil horizons. All this allows to reduce considerably norm of introduction of nutritious elements, to receiving high and qualitative a harvest and also maintaining fertility of soils.

IV. METHODOLOGY

Initial materials for receiving the organomineral of fertilizers of the containing humic substances and other products, are peat and the oxidized coal in nature. Coals with the content of humic acids higher than 45% are effectively used as raw materials for production of humic fertilizers and various humates. And coals with the content of humic acids to 20% need to be oxidized. In brown coal of the Angren field the content of humic acids is not enough. Therefore, we for transformation of an organic part of coal into humic acids studied oxidation process. In experiences the brown coal of the Angren field having after drying to air dry state and crushing in a spherical mill to the size of 0,25 mm structure was used (weight,%): moisture 14,1; ashes 13,7; organic chemistry 72,2; humic acids of 4,1% for organic weight. Process of oxidation of coal was carried out at concentration of nitric acid from 10 to 40%, temperature from 30 to 60ºC, lasting from 30 up to 120 min. and a weight ratio of an organic part of coal to monohydrate of nitric acid from 1:0,4 to 1:2. Under optimal conditions the oxidation level of coal was 65,5%. The received product of oxidation contains 57,2% of humic acids. After completion of oxidation of coal, the formed suspension was subjected to centrifugation. The firm phase was the dense mass of the oxidized coal. It contained organic matter 56,34%, humic acids in terms of organic weight of 58,54%, ashes of 3,28%, moisture of 40,38% and it pH 0,624 equaled. We used this damp dense mass of the oxidized coal as an initial component of the fertilizers received the organomineral [6].

It should be noted that after division into liquid and firm phases of the oxidized coal on liquid to a phase determined the content of free nitric acid for reuse as oxidizer by centrifuges. For this purpose, at first defined keeping of functional groups of water-soluble organic acids in a liquid phase. Functional groups revealed by the sorption method based on ability of the active sour groups which are contained in organic weight to react with chloride barium in the alkaline environment [7]. The amount of free nitric acid was determined by a method [8] with a deduction of a consumption of the sodium hydroxide spent when determining functional groups of water-soluble organic acids in a liquid phase. The amount of free nitric acid was 72,81% of the initial used nitric acid. The liquid phase, the nitric acid coal suspension received at a stage of centrifugation was applied to dilution of initial nitric acid to its concentration of 30% and it is used for oxidation of the following consignment of coal [9].

In works with us [9-11] were studied processes of receiving nitrogen-phosphorus-humic, phosphorus-humic, liquid and firm nitrogen-humic the organomineral of fertilizers on the basis of brown coal of the Angren field.

By oxidation of the Angren brown coal nitric acid and the subsequent decomposition of phosphorene's Central Kyzylkum anitric acid coal pulp received organomineral fertilizer of the following structure (weight, %): P_2O_{5gen}9,41; P_2O_{5acq}according to limit to – those 7,71; P_2O_{5acq} on 4,78; $CaO_{wat.}$ 11,27; N 7,75; organic matter 23,62 [10].

By mixture the phosphoric acidof pulps of the Kyzylkum phosphorene's with a product of oxidation of brown coal nitric acid received the phosphorus-humic fertilizers having the following structure (weight, %): P_2O_{5gen}– 16,96-32,36; P_2O_{5acq}according to limit to – they are 11,90-28,97; $P_2O_{5wat.}$ – 8,82-25,24; nitrogen – 4,25-4,56; $CaO_{acq.}$ – 5,15-8,37; humic substances – 14,34-25,54 [9].

Step oxidation of brown coal received liquid and solid nitrogen-humic fertilizers. The humate of ammonium allocated after the first step of oxidation of coal is used as additive to the liquid CAN nitrogen fertilizer (carbamide ammonium nitrate). The liquid fertilizers “Ammonium CAN-humate” with contents N from 15,15 to 29,42% and a humate of ammonium from 4.54 to 37.7% are received. By mixture of residual coal after oxidation with a carbamide the solid nitrogen-humic fertilizers containing N from 8,24 to 23,54%, organic matter from 40 to 67,57% and humic acids from 20,89 to 35,01% [11] are received.

On the basis of the conducted researches the technology of receiving the organomineral of fertilizers is developed. Trial tests with release of pilot batches the organomineral of fertilizers are carried out.

Agrochemical tests of the received fertilizers on the basis of the Angren brown coal and the Kyzylkum phosphorene's on a cotton and wheat showed that in comparison with control option the increase of a harvest makes 4.1 and 9,4 c/hectare respectively. Use of this fertilizer under cucumbers was increased by productivity by 17,9%, under tomatoes for 13,4%, under potatoes for 10,3%, and under cabbage for 23,6% [12-15].

The purpose of this work is receiving humic plain superphosphate containing nitrogen, the assimilable of forms of phosphorus, sulphur, calcium and humic substances.

It should be noted that in literature ways of receiving the organomineral of fertilizers on the basis of plain superphosphate and brown coals the oxidized environment are already known. From such coals containing not less than 40% of humic acids, in the early seventies at the Kokand superphosphate plant (The Kyrgyz “Kyzyl-Kia” coalfield,

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content of humic acids of 40,1%), at the plants of Irkutsk (Goose-Ozyorsk coalfield, content of humic acids more than 40%) large parties organomineral fertilizers for broad agrochemical tests were prepared. Receiving process, the organomineral of fertilizers consisted in mixture of one ton of dry coal with 50-100 liters of ammoniac water and 50-100 kg of unary superphosphate. Large-scale tests of these fertilizers were carried out in Ukraine, in Bashkiria, in Kyrgyzstan, in Uzbekistan and in Eastern Siberia. According to skilled institutions entering of brown coal into mixes with superphosphate or other mineral fertilizers raises a harvest: sugar beet on 15-40, buckwheat's - to 4, potatoes – to 46, corn (grain) – to 14 and a winter wheat up to 3-6 centers from hectare. The efficiency of combined use of brown coals with mineral fertilizers is established on all kinds of soils [16].

But in literature there are no data on use of the oxidized brown coal nitric acid of the Angren field in production of plain superphosphate.

For receiving humic plain superphosphate we used products of the Kyzylkum phosphoric plant, namely ordinary phosphoric flour. Structure of a phosphoric meal (weight, %): 17,32 P_2O_5; 47,56 CaO; 1,24 Al_2O_3; 1,05 Fe_2O_3; 1,75 MgO; 2,0 F; 16,0 CO_2; CaO: P_2O_5=2,69. For activation of phosphate raw materials sulfuric acid with concentration of 92% is used. As organic making it is used a firm phase of the oxidized coal of the above-stated structure.

V. EXPERIMENTAL RESULTS

At first activation of phosphate raw materials by sulfuric acid for the purpose of the translation of unavailable P_2O_5 form in raw materials in a form, assimilable for plants, was made. The norm of acid was taken in number of 40, 50, 60, 70, 80, 90 and 100% of a stoichiometryfor formation of the monocalsiumphosphat on reaction:

$$\text{CaO in a fossyrye} + 2H_2SO_4 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O$$

At norm of acid of 100% of a stoichiometryprocessing of 100 g of a phosphoric meal requires 77,5 g of H_2SO_4 with concentration of 92%. Processing of a fossyrye sulfuric acid was carried out within 60 min. At once upon completion of interaction of a fossyrye with sulfuric acid mixed in the oxidized coal, from the center fugirovate from nitric acid. It undertook in weight ratios phosphorene: coal (organic part of initial coal) =1:(0,05-1). Then the received mix was mixed within 30 min. and neutralized 25% water ammonia to values pH 4-4,5. Drying was carried out at 80□C, and granulation by an ocation method in the course of ammonization and drying. Defined the chemical composition and durability of granules of fertilizers. Durability of granules of 2-3 mm in size was determined by the measuring instrument of durability of granules IPG-1M, their average size was 2,2-2,4 MPs. Definition of all P_2O_5 forms carried out by a weight method by sedimentation phosphate ion magnesium mix in the form of phosphate magnesium ammonium with the subsequent calculating of a deposit at 1000-1050ºC according to state standard specification 20851,2-75. Nitrogen was defined in accordance with GOST by 26715-85. SO_3 determined by sedimentation in the form of sulfate of barium, the maintenance of CaO determined complexion metric by titration of 0,05 N solution of a triton of B in the presence of the indicator of a Fulkerson [17]. An exit of the humic acids (HA) – in accordance with GOST 9517-76. Results of the analysis are given in the table.

From tables it is visible that at identical weight ratios phosphorite: coal, the more norm of sulfuric acid, the more relative maintenance of assimilable P_2O_5 form and CaO in a product.

Table 1
The chemical composition of the fertilizers received the organomineral

Weight ratio coal: phosphorite	Moist ure %	P_2O_5gen., %	P_2O_5acq., %	CaO gen., %	CaO acq., %	$\frac{P_2O_{5усв.}}{P_2O_{5общ.}}$, %	SO_3, %	N, %	Org. mat.,%	HA., %
Norm of H_2SO_4 from a stoichiometry on educations $Ca(H_2PO_4)_2$, % 40										
1: 0	0,86	13,25	7,69	36,43	4,38	58,04	20,43	0,42	0	0
1: 0,05	1,09	12,06	7,06	34,58	4,26	58,54	18,59	0,78	3,49	1,57
1: 0,1	1,27	11,07	6,55	33,37	4,21	59,17	17,06	0,83	6,41	2,88
1: 0,25	1,67	8,98	5,42	30,48	4,04	60,36	14,88	1,38	12,23	5,48
1: 0,5	2,24	7,25	4,54	24,53	3,57	62,62	11,17	2,34	20,97	9,44

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1: 0,75	2,83	5,62	3,64	18,58	2,94	64,77	8,66	3,28	24,41	10,98
1: 1	3,39	4,59	3,09	12,62	2,16	67,32	7,07	4,27	26,54	11,94
Norm of H_2SO_4 from a stoichiometry on educations $Ca(H_2PO_4)_2$, % 50										
1:0	0,95	12,66	8,03	34,81	4,31	63,43	23,48	0,75	0	0
1: 0,05	1,17	11,87	7,61	33,38	4,16	64,11	21,98	0,88	3,43	1,54
1: 0,1	1,38	11,18	7,22	31,96	4,02	64,58	20,73	1,04	6,47	2,91
1: 0,25	1,76	9,24	6,08	29,19	3,93	65,80	17,11	1,52	11,27	5,07
1: 0,5	2,34	6,62	4,53	23,57	3,54	68,43	12,24	2,34	19,11	8,58
1: 0,75	2,94	5,38	3,78	17,95	2,98	70,26	9,96	3,13	23,26	10,47
1: 1	4,03	6,14	5,68	16,88	3,81	92,51	19,57	6,83	35,57	16,01
Norm of H_2SO_4 from a stoichiometry on educations $Ca(H_2PO_4)_2$, % 60										
1:0	1,01	12,13	8,48	33,35	4,38	69,91	26,56	1,44	0	0
1: 0,05	1,23	11,69	8,24	32,24	4,32	70,49	25,59	1,58	3,39	1,53
1: 0,1	1,41	11,28	8,02	31,12	4,26	71,09	24,71	1,75	6,53	2,94
1: 0,25	1,84	8,85	6,39	29,06	4,21	72,20	19,41	2,25	10,46	4,71
1: 0,5	2,42	6,06	4,52	24,77	3,81	74,59	13,27	3,06	17,54	7,89
1: 0,75	3,03	5,54	4,26	20,48	3,57	76,90	11,12	3,87	22,07	9,91
1: 1	3,87	5,86	5,11	16,11	3,54	87,20	22,15	6,14	44,96	20,23
Norm of H_2SO_4 from a stoichiometry on educations $Ca(H_2PO_4)_2$, % 70										
1:0	1,13	11,93	8,82	32,25	4,43	73,93	30,02	2,13	0	0
1: 0,05	1,34	11,45	8,52	31,23	4,37	74,41	28,78	2,28	3,36	1,49
1: 0,1	1,56	11,02	8,27	30,06	4,31	75,05	27,72	2,46	6,38	2,87
1: 0,25	1,94	9,33	7,12	25,44	4,22	76,31	23,18	2,98	12,08	5,44
1: 0,5	2,53	7,21	5,66	19,65	3,42	78,50	18,12	3,83	20,85	9,38
1: 0,75	3,12	6,32	5,13	17,17	3,28	81,17	15,84	4,68	27,35	12,31
1: 1	3,71	5,57	4,65	15,25	3,13	83,48	14,07	5,52	32,39	14,58
Norm of H_2SO_4 from a stoichiometry on educations $Ca(H_2PO_4)_2$, % 80										
1:0	1,24	11,71	9,13	32,19	5,24	77,97	33,39	2,79	0	0
1: 0,05	1,46	11,21	8,79	31,13	5,18	78,41	31,98	2,93	3,25	1,46
1: 0,1	1,68	10,71	8,45	30,06	5,06	78,90	30,73	3,02	6,22	2,78
1: 0,25	2,06	10,04	8,06	28,17	4,81	80,28	28,67	3,63	14,48	6,52

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1: 0,5	2,66	8,87	7,32	24,15	4,68	82,53	25,34	4,47	25,71	11,57
1: 0,75	3,27	8,28	7,02	20,13	4,19	84,78	23,64	5,31	35,97	16,19
1: 1	3,87	5,86	5,11	16,11	3,54	87,20	22,15	6,14	44,96	20,23
Norm of H_2SO_4 from a stoichiometry on educations $Ca(H_2PO_4)_2$, % 90										
1:0	1,33	11,45	9,54	31,48	5,61	83,32	36,54	3,41	0	0
1: 0,05	1,54	10,69	8,94	30,52	5,46	83,63	34,09	3,58	3,08	1,39
1: 0,1	1,85	10,03	8,46	29,56	5,34	84,35	31,94	3,74	5,81	2,62
1: 0,25	2,16	8,68	7,51	27,83	5,08	86,52	30,58	4,27	13,81	6,21
1: 0,5	2,78	8,49	7,46	24,18	4,82	87,87	27,06	5,12	24,58	11,04
1: 0,75	3,41	7,13	6,43	20,53	4,22	90,18	22,72	5,98	30,97	13,94
1: 1	4,03	6,14	5,68	16,88	3,81	92,51	19,57	6,83	35,57	16,01
Norm of H_2SO_4 from a stoichiometry on educations $Ca(H_2PO_4)_2$, % 100										
1:0	1,43	11,24	9,86	30,91	5,71	87,72	39,67	3,91	0	0
1: 0,05	1,66	10,23	9,03	29,78	5,56	88,28	36,03	3,97	2,96	1,33
1: 0,1	1,82	9,39	8,33	28,68	5,43	88,76	33,07	4,06	5,44	2,45
1: 0,25	2,68	9,18	8,25	26,68	5,03	89,87	32,54	4,41	13,24	5,94
1: 0,5	3,76	8,13	7,51	22,44	4,54	92,37	29,06	4,92	23,55	10,59
1: 0,75	3,97	6,25	5,92	18,21	4,36	94,72	22,08	5,43	27,16	12,23
1: 1	4,19	5,08	4,96	13,96	3,48	97,34	17,85	5,93	29,42	13,23

Content of organic matter, humic acids and $P_2O_{5gen.}$ goes down. So, at a ratio phosphorene: coal =1:0,5 and norm of sulfuric acid of 40% of a stoichiometry for formation of the monocalsiumphosphate we receive the organomineral fertilizer containing $P_2O_{5gen.}$ 7,25%; $P_2O_{5acq.}$ on citric acid of 4,54%, i.e. $P_2O_{5acq.}P_2O_{5gen.}$62,62%; 2,34% nitrogen; 20,97% organic matter; humic acids of 9,44%, $CaO_{gen.}$ 24,53%, $CaO_{acq.}$ 3,57% and SO_3 of general 11,17%. At the same ratio of coal to a phosphoric meal, but at norm of the last on formation of the monocalsiumphosphate of 100% the fertilizer containing $P_2O_{5gen.}$turns out 8,13%; $P_2O_{5acq.}$on citric acid of 7,51%, i.e. $P_2O_{5acq.}$: $P_2O_{5gen.}$ 92,37%; 4,92% nitrogen; 23,55% organic matter; humic acids of 10,59%, $CaO_{gen.}$22,44%, $CaO_{acq.}$4,54% and SO_3 of general 29,06%. From the table it is also visible that, with increase in norm of the oxidized coal the relative maintenance of assimilableP_2O_5 form increases. For example, at a ratio phosphorene: coal =1:0.05 and norm of sulfuric acid of 70% of a stoichiometryfor formation of the monocalsiumphosphate the relative maintenance of assimilable P_2O_5 form makes 74,41%, at same to norm of sulfuric acid on formation of the monocalsiumphosphate but at a ratio phosphorene: coal =1:1 relative maintenance of assimilable P_2O_5 form makes 83,48%.

Real time the mastered production technology of the ammoniated plain superphosphate consists of the following main stages. Decomposition of phosphate raw materials sulfuric acid at its norm from a stoichiometryof 100% and at a temperature 70-75ºC; chamber ripening of superphosphate weight during 1-1,5 h at a temperature 115-120ºC; warehouse ripening within 6 days at 3-times shoveling; granulation and ammonization (humidity of superphosphate before granulation of 14-15%); drying and paccев product. It should be noted that ammonization and drying of superphosphate weight leads to increase in the general P_2O_5 form in a product, but to reduction of assimilableP_2O_5 form due to course of the following of reaction [18].

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$$H_3PO_4 + NH_3 = NH_4H_2PO_4 \quad (1)$$
$$Ca(H_2PO_4)_2 + NH_3 = CaHPO_4 + NH_4H_2PO_4 \quad (2)$$
$$2CaHPO_4 + CaSO_4 + 2NH_3 = Ca_3(PO_4)_2\downarrow + (NH_4)_2SO_4 \quad (3)$$

From the obtained data of the real work it is visible that additions of the oxidized coal in sour superphosphate weight processed in various norms by sulfuric acid before ammonization and drying are led to considerable degree to increase by the relative maintenance of assimilable P_2O_5 form. Obviously, additions of the oxidized coal and consequently also humic acids shift reaction to formation of the monocalsiumphosphate and a humate of calcium aside, and it is led to increase in contents by the assimilable of the P_2O_5 to forms of reaction.

$$2R\ COOH + Ca(H_2PO_4)_2 = (R\ COO)_2\ Ca + 2H_3PO_4 \quad (4)$$
$$2CaHPO_4 + CaSO_4 + 2NH_3 + 4RCOOH = Ca(H_2PO_4)_2 + (NH_4)_2SO_4 + 2(RCOO)_2Ca \quad (5)$$

The assimilable of P_2O_5 forms tells increase about course of two last reactions at ammonization of sour superphosphate weight added the oxidized coal. On modern the requirement of agro culture, it is desirable that in complex fertilizer of contents relative contents the assimilableof forms of phosphoric connections was not to exchange of 50%. Therefore, for processing the private of a phosphoric meal we consider optimum norm of sulfuric acid of 60% of stoichiometric norm for formation of the monocalsiumphosphate and weight phosphorene ratios to oxidized coal (1:0,25), at which the fertilizer containing $P_2O_{5gen.}$ turns out 8,85%; $P_2O_{5acq.}$ on citric acid of 6,39%, i.e. $P_2O_{5acq.}$:$P_2O_{5gen.}$72,20%; 2,25% nitrogen; 10,46% organic matter; humic acids of 4,71%, $CaO_{gen.}$ 29,06%, $CaO_{acq.}$ 4,21%, SO_3 of general 19,41% with a durability of granules of 2,1 MPs.

VI. CONCLUSION AND FUTURE WORK

Thus, receiving humic plain superphosphate by addition of the oxidized coal in sour superphosphate weight before ammonization and drying on the one hand the assimilable of P_2O_5 forms will give the chance to significant increase in relative contents, with another will reduce norms of sulfuric acid for decomposition of phosphate raw materials. At use of humic plain superphosphate in agriculture, certainly, the maintenance of a humus in the soil will increase, the structure, physic mechanical properties of the soil considerably will improve. Due to keeping of all necessary plants of nutrients create a possibility of receiving more big and qualitative crops, nutritious properties of plants and their resilience to diseases increase.

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