

Humic Superphosphates Based On Phosphorites And Oxidized Local Coal

Ganiev Pirnazar,

*PhD student, Institute of general and inorganic chemistry of Uzbek Academy of Sciences,
Uzbekistan.*

Namazov Shafolat,

*Doctor of technical sciences, professor, academician, head of laboratory of Phosphate fertilizer,
Institute of general and inorganic chemistry of Uzbek Academy of Sciences, Uzbekistan.*

Usanboyev Najimuddin,

*Doctor of technical sciences (DSc), Leading Researcher of Phosphate fertilizer laboratory, Institute
of general and inorganic chemistry of Uzbek Academy of Sciences, Uzbekistan.*

Abstract

The article presents the results of a study of the processes of obtaining humic superphosphates by decomposing enriched phosphorites of the Central Kyzyl Kum: washed burnt concentrate, washed dried concentrate, ordinary phosmuki powder with sulfuric acid and the addition of oxidized coal from the Angren field with hydrogen peroxide. It was found that the addition of oxidized coal to an acidic superphosphate mass before ammoniation and drying leads to neither a decrease as usually occurs when superphosphate is obtained by decomposition of phosphorites with sulfuric acid followed by ammoniation and drying, but to a significant increase in the relative content of assimilated forms of P_2O_5 . The optimum norm (60%) of sulfuric acid and the weight ratio of phosphorite to oxidized coal (1: 0.25) were found. Highly effective humic superphosphates are obtained from all types of raw materials, even as poor as ordinary phosmuk.

Keywords: *phosphorite, washed dried concentrate, washed calcined concentrate, ordinary phosmuk, sulfuric acid, oxidized coal, humic acids, decomposition, ammonization.*

Introduction

To increase the efficiency of crop production, it is necessary to introduce the latest soil cultivation technologies, the use of high-yielding varieties, as well as the integrated use of mineral and organomineral fertilizers. The practice of agriculture and numerous agrochemical tests show that one of the main factors determining the receipt of a high and high-quality crop from plants and the preservation of soil fertility is the use of mineral fertilizers in combination with organic ones containing humic substances and humates. Mineral fertilizers incorporating humic substances and humates have a higher agrochemical efficiency. A particularly noticeable effect of their use was noted on humus-poor gray piles of earth and sandy soils, which the republic has [1-4].

Humic substances are dark brown or dark brown natural high molecular weight organic compounds of complex physicochemical structures that are formed in soils, peat, coal, and other natural bodies that are widespread in nature. There are several groups of humic substances: humic acids, soluble only in alkaline solutions; hematmelanic acids recovered from the crude residue of humic acids with ethyl alcohol; fulvic acids, soluble in water, alkaline, and acidic solutions; humine, practically insoluble and not extracted from natural bodies organic matter. All these substances except humine are the most mobile and reactive components of humic substances that are actively involved in chemical processes and ecosystems [5-9].

The basis of the skeleton of humic acid molecules is an aromatic system containing, as substituents, carboxylic (-COOH), hydroxyl (-OH), carbonyl (-C = O), methoxy (-OCH₃), phenolic and quinoid groups, and ether, ester, aldehyde groups. Among the oxygen-containing functional groups, hydroxyls predominate, followed by carboxyl groups. Humic acids, depending on pH, can be divided into several fractions with different molecular weights. However, all fractions contain almost the same functional groups, which indicates the commonality of their structure. Therefore, humic acids are not a clearly defined class of compounds, but represent a group of high molecular weight compounds having

a slightly different composition, but with a common type of structure and common properties. In chemical composition, these are high molecular weight aromatic and aliphatic hydroxycarboxylic acids, fragments of which are interconnected by oxygen and methylene bridges [10, 11].

The presence of functional groups in humic substances determines acid-base properties, participation in redox reactions and complex formation, as well as triple buffering ability (acid-base, redox, isotonic). The component composition is responsible for the hydrophilic-lipophilic balance of the molecules of humic substances. Humic substances as colloidal disperse systems have some specific properties, in particular, electron surface and surface-active, and these properties are strongly influenced by the content of functional groups and the chemical composition of humic substances [10,11,6].

The elemental composition of humic acids is not the same: 57.5-64.2% - C; 4.3-5.4% - H; 29-34% - O; up to 4% - N. Nitrogen is a part of melanoids - condensation products of carbohydrate fragments with amino acids formed during the breakdown of proteins and carbohydrates. Variations in elemental composition depend on the nature of the initial biomass, in particular lignins. The genetic connection of humic acids with lignin has been established. With the gradual destruction of lignin by fungi (white and brown rot), some of the simplest compounds (fragments of molecules) are included in the metabolism of microorganisms, and high molecular humic substances are formed from the rest. In the case of a destructive process (bora rot), humic and hematmelanic acids are formed, with corrosion failure (white rot) - fulvic acids [12].

Humic substances in soils carry out various functions, giving the soil stable characteristics, determining many of their most important properties and functions, the main of which are accumulative, transport, regulatory, protective, and physiological.

The accumulative function is characteristic especially for humic acids. The essence of this function is the accumulation in the form of humic substances of the most important nutrients of living organisms, organic compounds that carry energy reserves, or are directly necessary and absorbed by microorganisms or plants. It is well known that it is in the form of humic substances in soils that up to 90-99% of all nitrogen, half or more of phosphorus, and sulfur is accumulated. In the same form, potassium, calcium, magnesium, iron and almost all trace elements necessary for microorganisms accumulate and remain for a long time.

The transport function of humic acids is that humic acids, along with sparingly soluble, stable compounds with metal cations, can also form stable, but soluble and capable of geochemical migration compounds. It is well known that at normal pH values for most soils, iron is almost immobile. The dominant form of iron hydroxide with the solubility product cannot cause a noticeable movement of ionic iron in the soil profile. However, iron migration is a well-established fact. For iron, as well as for cations of many other metals, the dominant migration form is represented by complex organomineral compounds, in which the role is played mainly by fulvic acids. Most trace elements, a significant part of phosphorus and sulfur compounds, actively migrate in this form.

The regulatory function of humic substances is complex. It combines many phenomena and processes in soils. In the regulatory function of humic substances, several main components are distinguished: 1) the formation of the soil structure and water-physical properties of soils; 2) regulation of the ion exchange reaction between solid and liquid phases; 3) the effect on acid-base and redox regimes; 4) regulation of the nutritional conditions of living organisms; 5) regulation of the thermal regime of soils and the atmosphere.

The protective function of humic substances is known, but not well understood. In general form, it can be argued that humic substances in the soil protect or preserve biota, pores in the event of various kinds of adverse extreme situations. Humic substances quite firmly bind many radionuclides, detergents, pesticides, thereby preventing their entry into plants or other negative effects. The physiological function is associated with the role of humic substances as carriers of essential amino acids, certain vitamins, and antibiotics. [13-15].

The effect of humic substances on the physiological activity of plants is diverse. It was shown in [16–22] that humic substances can enter the plant organism when they contain thousandths and ten-thousandths of a percent in the soil solution. Under the action of humic substances in plants, root formation is activated, due to a change in the selectivity of cell membranes, the flow of water and nutrients is increased, that humic compounds positively affect all phases of the mitotic cycle of cells and cause a 1.5-fold increase in the value of the mitotic index. They can participate in physiological and biochemical processes, activating the activity of enzymes of redox reactions, increasing respiration

rate, photosynthesis productivity, absorption of mineral elements, and the use of absorbed phosphorus for the synthesis of protein substances. The effect of such compounds is most actively manifested when external conditions deviate from the norm, in particular, mineral nutrition conditions, fluctuations in air and soil temperature, moisture, and oxygen content in the air and root sphere. Under extreme conditions, when the course of bioenergetic processes is disrupted and cannot be restored without additional energy expenditures, their adaptogenic ability manifests itself, which regulates the synthesis of nucleic acids, enzyme proteins, and constituent proteins, repair, and regeneration processes.

Thus, humic substances or humates, which are part of mineral fertilizers, contribute to better assimilation by plants of the basic nutrients. They contain microelements, physiologically and growth stimulating substances, form a loose soil structure, and stimulate the growth and development of plants. Humic acids in the form of water-soluble forms take an active part in the oxidation-reduction processes of the cell, being, on the one hand, a source of activated oxygen and, on the other, an acceptor of hydrogen. Increases plant resistance to adverse environmental factors: excessive doses of mineral fertilizers at high or low temperatures, chemical plant protection products. They also absorb nutrients and moisture, while reducing the possibility of leaching of nutrients in the subsoil horizons. All this allows to significantly reduce the dose of mineral fertilizers in the soil, to increase productivity, product quality, and soil fertility [23,24]. In this regard, the study of processes and the development of technology for producing mineral fertilizers, incorporating humic substances and humates, are relevant.

Materials and methods

This work aims to study the processes of obtaining granular humic superphosphates based on decomposed phosphorites of the Central Kyzyl Kum with sulfuric acid in various forms and of oxidized coal with hydrogen peroxide in an alkaline environment depending on the weight ratios of the starting components.

The main raw materials for humic fertilizers are peat and oxidized coal in natural conditions. Coals with a humic acid content above 45% are effectively used as raw materials for the production of humic fertilizers. And coal with a humic acid content of up to 20% must be oxidized. The brown coal of the Angren Deposit contains very little humic acids. Therefore, to convert the organic part of coal into humic acids, we studied the oxidation process. The experiments used brown coal from the Angren Deposit, which after drying to an air-dry state and grinding in a ball mill to a size of 0.25 mm, has the following composition (weight%): moisture 15.66; ash 12.11; organic 72.23; humic acids 4.24% per organic mass. The oxidation process was carried out at a concentration of hydrogen peroxide from 10 to 30%, a solution of sodium hydroxide from 20 to 40% and a weight ratio of coal (organic part): H₂O₂: NaOH from 1: 0.1: 0.05 to 1: 1: 0, 05. First, the coal was processed in a mechanical mortar with a solution of NaOH at a ratio of coal: NaOH from 1: 0.05 for 30 minutes. Then, the obtained mass was added to the tubular reactor, where the hydrogen peroxide solution was filled in advance and processed for 2 hours. Under optimal conditions, the content of humic acids was 61.42% based on the organic mass of oxidized coal obtained using 30% hydrogen peroxide, 40% sodium hydroxide and the mass ratio of coal (organic part of coal): H₂O₂: NaOH = 1: 0, 6: 0.05. After the completion of coal oxidation, the formed mass was a thick mass of oxidized coal. It contained organic substances 47.34%, humic acid in terms of organic mass 50.54%, ash 7.28%, moisture 45.38% [25].

To obtain humic superphosphates, the products of the Kyzylkum phosphorite plant were used, namely, washed dried concentrate (WDC), washed calcined concentrate (WCC), and ordinary phosphorite flour (OPF) whose compositions are shown in table 1. Sulfuric acid with a concentration of 92% was used to activate phosphate raw materials. The organic component used is oxidized coal of the above composition.

Table 1.

The chemical composition of phosphorites of the Central Kyzylkum

Types of phosphate raw materials	The content of components, weight. %								$\frac{P_2O_{5\text{óná.}}}{P_2O_{5\text{íáá.}}} \times 100, \%$	CaO : P ₂ O ₅
	P ₂ O ₅	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	F	CO ₂	H. o.		
The WCC	27,26	53,36	0,61	0,51	1,30	2,91	2,41	5,95	12,24	1,96

WDC	18,22	47,28	0,99	0,60	1,18	2,29	14,90	6,81	17,80	2,60
OPF	17,20	46,22	1,75	1,05	1,24	2,00	16,00	7,69	18,50	2,69

First, phosphate raw materials were activated with sulfuric acid to convert the non-digestible form of P₂O₅ into raw materials into a digestible form for plants. The acid rate was taken in an amount of 40, 50, 60, 70, 80, 90, and 100% of the stoichiometry for the formation of monocalcium phosphate by the reaction:



With an acid rate of 100% of stoichiometry, processing of 100 g of OPF requires 77.5 g of H₂SO₄ with a concentration of 92%. Processing fossy with sulfuric acid was carried out for 60 minutes. Immediately upon completion of the interaction of fossy with sulfuric acid, oxidized coal was introduced into the mixture. It was taken in the weight ratios of phosphorite: coal (organic part of the source coal) = 1: (0.05-1). Then the resulting mixture was stirred for 30 min and neutralized with 25% aqueous ammonia to pH values of 4-4.5. Drying was carried out at 80 ° C, and granulation by the method of rolling in the process of ammonization and drying. The chemical composition and strength of the fertilizer granules were determined. The strength of granules with a size of 2-3 mm was determined using an IPG-1M granule strength meter; their average value was 2.2-2.4 MPa. All P₂O₅ forms were determined by the gravimetric method by precipitation of the phosphate ion with a magnesia mixture in the form of magnesium ammonium phosphate, followed by calcination of the precipitate at 1000-1050 ° C according to GOST 20851.2-75. Nitrogen was determined according to GOST 26715-85. SO₃ was determined by precipitation in the form of barium sulfate, the CaO content was determined by titration with a 0.05 N solution of Trilon B in the presence of a flurexone indicator [26]. The output of humic acids (HA) is according to GOST 9517-76. The results of the analysis are shown in tables 2-4.

Results and discussions

The picture for all three types of phosphate raw materials is similar. The higher the norm of sulfuric acid and the less phosphate raw material taken, the less P₂O₅gen. in the product, but the greater the relative content of the assimilable form of P₂O₅. As can be seen from Table 2, when the

Table 2. The composition of humic superphosphates obtained based on oxidized coal and washed calcined phosphorite concentrate in Central Kyzylykum

Coal ratio: WCC	Moisture %	P ₂ O ₅ gen., %	P ₂ O ₅ acq. limt. %	P ₂ O ₅ acq. Tr.B., %	CaO gen., %	CaO acq., %	$\frac{P_2O_{5acq.}}{P_2O_{5gen.}}$, %	SO ₃ , gen %	N, gen %	Org. mat, %	HA... %
H ₂ SO ₄ norm from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 40											
1: 0	0,96	21,51	10,95	10,01	38,45	4,79	50,91	19,12	1,05	0	0
1: 0,05	1,09	20,45	10,51	9,60	37,46	4,79	51,39	18,14	1,12	3,72	1,67
1: 0,1	1,17	20,04	10,39	9,46	36,94	4,82	51,85	17,89	1,33	7,27	3,27
1: 0,25	1,37	17,55	9,36	8,49	32,18	4,48	53,33	15,58	1,44	15,61	7,02
1: 0,5	1,54	14,26	7,92	7,15	26,15	3,91	55,54	12,67	1,97	29,27	13,17
1: 0,75	1,73	11,75	6,81	6,08	21,56	3,06	57,96	10,44	2,22	31,27	14,07
1: 1	2,09	10,27	6,17	5,47	18,82	2,91	60,08	9,12	2,04	36,39	16,38
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 50											
1: 0	1,05	19,72	11,41	10,44	36,15	4,74	57,86	21,55	0,74	-	-
1: 0,05	1,18	19,43	11,32	10,34	35,64	4,72	58,26	21,24	0,88	3,54	1,59
1: 0,1	1,27	18,58	10,92	9,95	34,06	4,58	58,77	20,31	1,04	6,71	3,02
1: 0,25	1,48	16,37	9,84	8,93	30,02	4,31	60,11	17,89	1,16	14,56	6,55
1: 0,5	1,73	13,35	8,34	7,49	24,49	3,88	62,47	15,01	1,41	28,67	12,92
1: 0,75	2,07	11,41	7,39	6,58	20,92	3,47	64,77	12,47	1,64	30,34	13,65
1: 1	2,43	9,96	6,68	5,91	18,25	3,18	67,07	10,87	1,95	35,29	15,88

Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 60											
1: 0	1,16	18,76	12,04	11,09	34,41	4,88	64,18	24,35	1,38	-	-
1: 0,05	1,33	18,01	11,62	10,71	32,99	4,76	64,59	23,36	1,18	3,29	1,48
1: 0,1	1,57	17,54	11,41	10,46	32,16	4,71	65,05	22,76	1,62	6,33	2,85
1: 0,25	1,98	15,71	10,45	9,57	28,81	4,36	66,52	20,39	1,97	13,98	6,29
1: 0,5	2,32	12,85	8,84	8,03	23,56	3,76	68,79	16,67	2,09	27,85	12,54
1: 0,75	2,69	10,81	7,63	6,92	19,81	3,54	70,58	14,02	2,21	28,75	12,94
1: 1	3,14	9,54	6,96	6,24	17,49	3,37	72,96	12,59	2,29	33,81	15,22
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 70											
1: 0	1,33	17,83	12,97	12,23	32,69	4,92	72,74	26,72	1,97	-	-
1: 0,05	1,54	17,05	12,48	11,74	31,27	4,81	73,20	25,57	2,02	3,11	1,40
1: 0,1	1,76	16,34	12,03	11,30	29,96	4,72	73,62	24,51	2,09	5,89	2,65
1: 0,25	2,14	14,82	11,11	10,37	27,17	4,58	74,97	22,21	2,21	13,18	5,93
1: 0,5	2,75	12,28	9,47	8,77	22,53	4,19	77,12	18,42	2,43	21,77	9,81
1: 0,75	3,36	10,47	8,31	7,63	19,19	3,89	79,37	15,69	2,62	27,84	12,53
1: 1	3,81	9,32	7,59	6,93	17,11	3,74	81,44	13,98	2,87	33,05	14,87
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 80											
1: 0	1,44	19,73	15,71	14,77	31,06	4,98	79,62	28,91	2,46	0	0
1: 0,05	1,68	19,44	15,51	14,58	29,72	4,89	79,78	27,65	2,48	2,95	1,33
1: 0,1	1,91	18,58	14,85	13,95	29,12	4,87	79,92	27,08	2,58	5,73	2,58
1: 0,25	2,36	16,37	13,34	12,46	25,11	4,62	81,49	23,35	2,78	12,18	5,48
1: 0,5	2,96	13,35	11,15	10,36	21,69	4,33	83,52	20,17	3,03	20,96	9,43
1: 0,75	3,67	11,41	9,80	9,04	18,87	4,09	85,89	17,47	3,31	27,24	12,26
1: 1	4,37	9,96	8,68	7,98	16,68	3,86	87,15	15,52	3,63	32,24	14,51

continuation of table 2

Coal weight ratio: WCC	Moistur e%	P ₂ O ₅ gen., %	P ₂ O ₅ acq. limt. %	P ₂ O ₅ acq. Tr.B., %	CaO gen., %	CaO acq., %	$\frac{P_2O_{5acq.}}{P_2O_{5gen.}}$, %	SO ₃ , gen %	N, gen %	Org. mat, %	HA... %
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 90											
1: 0	1,56	16,11	13,92	13,11	29,53	5,30	86,41	30,81	2,94	0	0
1: 0,05	1,78	15,47	13,41	12,63	28,37	5,23	86,68	29,59	3,04	2,82	1,27
1: 0,1	2,08	14,91	12,96	12,22	27,32	5,18	86,92	28,51	3,06	5,38	2,42
1: 0,25	2,46	12,73	11,20	10,50	23,34	4,68	87,98	24,34	3,14	11,32	5,09
1: 0,5	2,98	11,41	10,27	9,58	20,91	4,55	90,01	21,82	3,28	20,22	9,11
1: 0,75	3,82	9,93	9,22	8,52	18,22	4,26	92,85	19,01	3,45	26,43	11,92
1: 1	4,93	8,81	8,31	7,65	16,14	4,02	94,32	16,84	3,81	31,21	14,04
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 100											
1: 0	1,67	15,37	14,61	13,65	28,18	5,63	95,06	32,52	3,34	0	0
1: 0,05	1,85	14,81	14,12	13,19	27,15	5,57	95,34	31,33	3,36	2,71	1,24
1: 0,1	2,05	14,32	13,71	12,78	26,26	5,52	95,74	30,31	3,44	5,14	2,31

1: 0,25	2,86	12,81	12,37	11,52	23,49	5,32	96,57	27,12	3,52	11,41	5,13
1: 0,5	3,95	10,96	10,67	9,91	20,11	4,71	97,35	23,21	3,71	19,43	8,75
1: 0,75	4,97	9,59	8,04	9,06	17,58	4,25	98,96	20,28	3,88	25,52	11,48
1: 1	5,87	8,65	7,30	8,37	15,84	3,97	99,77	18,25	4,14	30,62	13,78

ratio of coal: phosphorite = 1: 0.25 and the norm of sulfuric acid is 40% of the stoichiometry for the formation of monocalcium phosphate, humic superphosphate is obtained having the composition (wt.%): $P_2O_{5gen.}$ - 17.55; $P_2O_{5acq.}$ for citric acid - 9.36; $P_2O_{5acq.}$ for Trilon B - 8.49; organic matter - 15.61; humic acids - 7.02; nitrogen - 1.44; ; $CaO_{gen.}$ -32.18; relative contents of $P_2O_{5acq.}$ for citric acid - 53.33. At the same ratio of coal to phosphorus, but at the rate of the latter 100% of the stoichiometry for the formation of monocalcium phosphate, a fertilizer with a composition (weight. %): $P_2O_{5gen.}$ - 12.81; $P_2O_{5acq.}$ for citric acid-12.37; ; $P_2O_{5acq.}$ for Trilon B-11.52; organic substances-11.41; humic acids-5.13; nitrogen-3.52; $CaO_{gen.}$ -23.49; relative contents of $P_2O_{5gen.}$ for citric acid-96.57, i.e. the assimilable form of phosphorus is approximately 2 times increased. The table also shows that, with an increase in the amount of oxidized coal, the relative content of the digested form of P_2O_5 . increases.

For example, when the ratio phosphorite: coal = 1: 0.05 and the norm of sulfuric acid is 60% of the stoichiometry for the formation of monocalcium phosphate, the relative content of the assimilable form of P_2O_5 is 64.59%, with the same rate of sulfuric acid for the formation of monocalcium phosphate, but with the ratio of phosphorite: coal = 1: 1, the relative content of the assimilable form of P_2O_5 is 72.96%. Humic superphosphates of similar composition are also obtained by processing WDCs of phosphorites of the Central Kyzyl Kum (table 3).

Table 3. Composition of humic superphosphates obtained on the basis of oxidized coal with hydrogen peroxide and washed dried concentrate of phosphorites of the Central Kyzyl Kum

Coal weight ratio: WDC	Moisture %	P_2O_5 gen., %	P_2O_5 acq. limit. %	P_2O_5 acq. Tr.B., %	CaO gen., %	CaO acq., %	$\frac{P_2O_{5acq.}}{P_2O_{5gen.}}$, %	SO ₃ , gen %	N, gen %	Org. mat, %	HA... %
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 40											
1: 0	0,98	17,62	8,61	7,08	32,05	4,42	48,86	18,96	1,48	0	0
1: 0,05	1,17	16,78	8,29	6,78	30,41	4,24	49,40	18,04	1,53	4,03	1,82
1: 0,1	1,38	15,94	7,94	6,46	28,76	4,06	49,81	17,15	1,68	7,28	3,28
1: 0,25	1,76	13,68	7,02	5,63	24,12	3,61	51,32	15,63	1,84	10,54	4,74
1: 0,5	2,38	11,41	6,11	4,81	19,48	3,06	53,55	12,26	2,28	17,35	7,81
1: 0,75	2,95	8,31	4,64	3,59	13,18	2,15	55,84	8,92	3,66	24,01	10,76
1: 1	3,38	5,19	3,02	2,29	6,19	1,26	58,19	5,56	4,08	30,67	13,78
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 50											
1: 0	1,02	16,78	9,36	8,56	29,72	4,47	55,78	23,32	2,25	0	0
1: 0,05	1,25	15,98	8,99	8,19	28,21	4,32	56,26	21,44	2,28	3,84	1,73
1: 0,1	1,47	14,18	8,05	7,34	26,71	4,18	56,77	20,56	2,34	7,05	3,16
1: 0,25	1,87	13,05	7,59	6,88	22,43	3,83	58,16	19,05	2,62	10,26	4,62
1: 0,5	2,43	10,91	6,60	5,94	18,15	3,31	60,49	15,78	3,08	16,91	7,61
1: 0,75	3,04	7,97	5,01	4,46	12,36	2,38	62,86	11,53	3,45	23,44	10,55
1: 1	3,51	4,03	2,62	2,32	6,57	1,32	65,01	7,28	3,82	29,97	13,46
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 60											
1: 0	1,13	15,94	10,09	9,22	27,38	4,58	63,30	25,72	2,93	0	0
1: 0,05	1,35	15,17	9,67	8,76	26,01	4,42	63,74	24,13	2,96	3,68	1,67
1: 0,1	1,58	13,43	8,64	7,88	24,64	4,24	64,33	22,54	3,02	6,83	3,07
1: 0,25	1,84	12,44	8,19	7,41	20,73	3,73	65,84	21,52	3,17	9,92	4,46

1: 0,5	2,54	10,44	7,13	6,41	18,81	3,54	68,30	17,31	3,41	16,52	7,43
1: 0,75	3,08	7,64	5,42	4,77	11,52	2,26	70,94	13,11	4,68	22,94	10,32
1: 1	3,64	3,84	2,82	2,45	7,23	1,28	73,44	8,89	4,98	29,35	13,21
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 70											
1: 0	1,25	14,78	10,46	9,66	24,38	4,33	70,77	28,21	3,47	0	0
1: 0,05	1,46	14,08	10,02	9,25	23,15	4,16	71,16	27,04	3,51	3,47	1,56
1: 0,1	1,68	13,01	9,32	8,58	21,91	4,04	71,64	25,86	3,56	5,59	2,52
1: 0,25	2,07	11,94	8,71	7,94	18,47	3,47	72,95	23,73	3,75	9,66	4,35
1: 0,5	2,61	9,97	7,49	6,71	15,02	2,86	75,13	19,24	3,92	15,85	7,13
1: 0,75	3,22	7,12	5,50	4,92	10,34	2,05	77,25	14,76	4,04	17,04	7,67
1: 1	3,73	3,56	2,82	2,56	5,66	1,17	79,21	10,27	4,26	28,23	12,68

continuation of table 3

Coal weight ratio: WDC	Moist ure%	P ₂ O ₅ gen., %	P ₂ O ₅ acq. limt. %	P ₂ O ₅ acq. Tr.B., %	CaO gen., %	CaO acq., %	$\frac{P_2O_{5acq.}}{P_2O_{5gen.}}$, %	SO ₃ , gen %	N, gen %	Org. mat, %	HA... %
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 80											
1: 0	1,34	13,02	10,09	9,43	21,38	3,88	77,50	30,02	3,91	0	0
1: 0,05	1,53	12,72	9,88	9,22	20,27	3,71	77,67	28,95	3,93	3,23	1,46
1: 0,1	1,77	11,42	8,90	8,30	19,21	3,59	77,93	27,88	3,98	6,16	2,77
1: 0,25	2,26	10,58	8,31	7,75	16,22	3,16	78,54	25,98	4,02	9,08	4,09
1: 0,5	2,72	8,04	6,39	5,96	13,23	2,76	79,48	21,94	4,18	15,19	6,84
1: 0,75	3,35	6,02	4,93	4,54	9,16	2,01	81,89	17,91	4,33	21,17	9,53
1: 1	3,98	3,06	2,60	2,38	5,08	1,13	84,97	13,87	4,48	27,15	12,22
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 90											
1: 0	1,44	12,45	10,48	9,94	20,71	4,03	84,18	31,32	4,26	0	0
1: 0,05	1,64	11,23	9,50	8,98	19,64	3,87	84,59	30,08	4,27	3,01	1,35
1: 0,1	1,75	10,21	8,67	8,18	18,58	3,73	84,92	28,88	4,28	4,41	1,98
1: 0,25	2,36	9,43	8,11	7,62	15,63	3,41	86,00	26,64	4,32	8,83	3,96
1: 0,5	2,98	7,24	6,37	5,93	12,67	2,83	87,98	21,96	4,41	14,65	6,59
1: 0,75	3,51	5,13	4,60	4,26	8,65	2,22	89,67	17,28	4,57	20,47	9,21
1: 1	4,09	2,02	1,84	1,70	4,63	1,56	91,09	12,61	4,66	26,28	11,83
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ , % 100											
1: 0	1,54	11,27	10,37	9,90	20,03	4,21	92,01	32,05	4,51	0	0
1: 0,05	1,75	10,76	9,94	9,47	19,05	4,09	92,38	30,84	4,52	2,72	1,21
1: 0,1	1,91	9,24	8,56	8,15	18,06	3,97	92,64	29,64	4,53	5,34	2,38
1: 0,25	2,47	8,89	8,32	7,89	15,09	3,68	93,59	27,45	4,55	12,31	5,54
1: 0,5	3,55	6,53	6,23	5,87	12,12	3,05	95,41	22,84	4,61	19,28	8,64

1: 0,75	4,02	4,64	4,49	4,21	8,14	2,36	96,77	18,24	4,66	22,32	10,02
1: 1	4,96	1,78	1,75	1,63	4,17	1,72	98,31	13,64	4,74	25,36	11,41

Naturally, from OPF fertilizers are obtained that are relatively poorer in phosphorus than WCC and WDC (Table 4). So, when using OPF at the ratio of coal: phosphorite = 1: 0.25 and the norm of sulfuric acid is 60 % of the stoichiometry for the formation of monocalcium phosphate is obtained humic superphosphate having a composition (wt.%): P₂O_{5gen.} - 10.62; P₂O_{5acq.} for citric acid-7.67; P₂O_{5gen.} for Trilon B-6.63; organic substances-10.46; humic acids-4.71; nitrogen-1.89; CaO_{gen.} -29.06; relative contents of P₂O_{5acq.} for citric acid-72.22. And at the rate of acid 80% with the same ratio of coal: phosphorite, the fertilizer contains P₂O_{5gen.} - 10.58; P₂O_{5acq.} for citric acid-8.31; P₂O_{5acq.} for Trilon B - 7.75; organic substances-9.08; humic acids-4.09; nitrogen-4.02; CaO_{gen.} -16.22; relative contents of P₂O_{5acq.} for citric acid - 78.54.

Table 4. Composition of humic superphosphates obtained on the basis of oxidized coal with hydrogen peroxide and ordinary fosmuki of the Central Kyzyl Kum

Coal ratio: OPF	Moisture re%	P ₂ O ₅ gen., %	P ₂ O ₅ acq. limt. %	P ₂ O ₅ acq. Tr.B., %	CaO gen., %	CaO acq., %	$\frac{P_2O_{5acq.}}{P_2O_{5gen.}}$, %	SO ₃ , gen %	N, gen %	Org. mat, %	HA... %
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 40											
1: 0	0,86	14,38	8,35	7,32	36,43	4,38	58,07	20,43	0,42	0	0
1: 0,05	1,09	13,57	7,94	6,91	34,58	4,26	58,51	18,59	0,58	3,49	1,57
1: 0,1	1,27	12,86	7,61	6,58	33,37	4,21	59,18	17,06	0,63	6,41	2,88
1: 0,25	1,67	11,48	6,93	5,92	30,48	4,04	60,37	14,88	0,98	12,23	5,48
1: 0,5	2,24	10,12	6,34	5,33	24,53	3,57	62,65	11,17	1,34	20,97	9,44
1: 0,75	2,83	8,76	5,67	4,66	18,58	2,94	64,73	8,66	1,88	24,41	10,98
1: 1	3,39	7,39	4,97	3,95	12,62	2,16	67,25	7,07	2,27	26,54	11,94
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 50											
1: 0	0,95	13,86	8,79	7,73	34,81	4,31	63,43	23,48	0,75	0	0
1: 0,05	1,17	13,12	8,38	7,36	33,38	4,16	64,11	21,98	0,88	3,43	1,54
1: 0,1	1,38	12,46	8,04	7,01	31,96	4,02	64,58	20,73	1,04	6,47	2,91
1: 0,25	1,76	11,08	7,29	6,25	29,19	3,93	65,80	17,11	1,42	11,27	5,07
1: 0,5	2,34	9,72	6,65	5,64	23,57	3,54	68,43	12,24	1,84	19,11	8,58
1: 0,75	2,94	8,35	5,87	4,81	17,95	2,98	70,26	9,96	2,13	23,26	10,47
1: 1	4,03	6,98	5,07	4,04	16,88	3,81	92,51	19,57	2,83	35,57	16,01
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 60											
1: 0	1,01	13,33	9,12	8,16	33,35	4,38	69,91	26,56	1,44	0	0
1: 0,05	1,23	12,64	8,81	7,76	32,24	4,32	70,49	25,59	1,58	3,39	1,53
1: 0,1	1,41	12,02	8,51	7,45	31,12	4,26	71,09	24,71	1,65	6,53	2,94
1: 0,25	1,84	10,62	7,67	6,63	29,06	4,21	72,22	19,41	1,89	10,46	4,71
1: 0,5	2,42	9,23	6,88	5,82	24,77	3,81	74,59	13,27	3,06	17,54	7,89
1: 0,75	3,03	7,83	6,03	5,01	20,48	3,57	76,90	11,12	3,67	22,07	9,91
1: 1	3,87	6,43	5,09	4,05	16,11	3,54	87,20	22,15	4,14	44,96	20,23
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 70											
1: 0	1,13	12,83	9,49	8,44	32,25	4,43	73,93	30,02	2,13	0	0
1: 0,05	1,34	12,31	9,16	8,12	31,23	4,37	74,41	28,78	2,18	3,36	1,49
1: 0,1	1,56	11,74	8,81	7,76	30,06	4,31	75,05	27,72	2,26	6,38	2,87
1: 0,25	1,94	10,35	7,83	6,82	25,44	4,22	76,31	23,18	2,38	12,08	5,44
1: 0,5	2,53	8,96	7,04	6,02	19,65	3,42	78,50	18,12	2,63	20,85	9,38

1: 0,75	3,12	7,57	6,14	5,13	17,17	3,28	81,17	15,84	2,88	27,35	12,31
1: 1	3,71	6,17	5,16	4,19	15,25	3,13	83,48	14,07	3,22	32,39	14,58

continuation of table 4

Coal weight ratio: OPF	Moisture re%	P ₂ O ₅ gen., %	P ₂ O ₅ acq. limt. %	P ₂ O ₅ acq. Tr.B., %	CaO gen., %	CaO acq., %	$\frac{P_2O_{5acq.}}{P_2O_{5gen.}}$, %	SO ₃ , gen %	N, gen %	Org. mat, %	HA... %
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 80											
1: 0	1,24	12,31	9,60	8,54	32,19	5,24	77,97	33,39	2,79	0	0
1: 0,05	1,46	11,73	9,21	8,24	31,13	5,18	78,41	31,98	2,83	3,25	1,46
1: 0,1	1,68	11,18	8,83	7,79	30,06	5,06	78,90	30,73	2,92	6,22	2,78
1: 0,25	2,06	9,85	7,91	6,88	28,17	4,81	80,28	28,67	3,03	14,48	6,52
1: 0,5	2,66	8,52	7,03	6,01	24,15	4,68	82,53	25,34	3,27	25,71	11,57
1: 0,75	3,27	7,19	6,11	5,08	20,13	4,19	84,78	23,64	3,41	35,97	16,19
1: 1	3,87	5,86	5,12	4,16	16,11	3,54	87,20	22,15	3,64	44,96	20,23
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 90											
1: 0	1,33	11,76	9,81	8,76	31,48	5,61	83,32	36,54	3,41	0	0
1: 0,05	1,54	11,23	9,39	8,34	30,52	5,46	83,63	34,09	3,45	3,08	1,39
1: 0,1	1,85	10,74	9,06	8,01	29,56	5,34	84,35	31,94	3,51	5,81	2,62
1: 0,25	2,16	9,39	8,13	7,11	27,83	5,08	86,52	30,58	3,57	13,81	6,21
1: 0,5	2,78	8,04	7,06	6,04	24,18	4,82	87,87	27,06	3,82	24,58	11,04
1: 0,75	3,41	6,69	6,04	5,03	20,53	4,22	90,18	22,72	4,08	30,97	13,94
1: 1	4,03	5,34	4,94	3,88	16,88	3,81	92,51	19,57	4,23	35,57	16,01
Norm H ₂ SO ₄ from stoichiometry on formations Ca(H ₂ PO ₄) ₂ . % 100											
1: 0	1,43	11,24	9,86	8,82	30,91	5,71	87,72	39,67	3,91	0	0
1: 0,05	1,66	10,23	9,03	8,01	29,78	5,56	88,28	36,03	3,94	2,96	1,33
1: 0,1	1,82	9,39	8,33	7,36	28,68	5,43	88,76	33,07	4,01	5,44	2,45
1: 0,25	2,68	9,18	8,25	7,21	26,68	5,03	89,87	32,54	4,09	13,24	5,94
1: 0,5	3,76	8,13	7,51	6,46	22,44	4,54	92,37	29,06	4,22	23,55	10,59
1: 0,75	3,97	6,25	5,92	4,88	18,21	4,36	94,72	22,08	4,38	27,16	12,23
1: 1	4,19	5,08	4,96	3,92	13,96	3,48	97,34	17,85	4,53	29,42	13,23

It should be noted that, at present, the mastered production technology of ammoniated simple superphosphate consists of the following main stages. Decomposition of phosphate raw materials by sulfuric acid at its norm from stoichiometry of 100% and at a temperature of 70-75 ° C; chamber maturation of superphosphate mass for 1-1.5 hours at a temperature of 115-120 ° C; warehouse maturation for 6 days with 3 single shoveling; granulation and ammonization (humidity of

superphosphate before granulation 14-15%); drying and sieving of the product. It should be noted that ammonization and drying of superphosphate mass leads to an increase in the general form of P_2O_5 in the product, but a decrease in the assimilable form of P_2O_5 due to the retrograde phosphorus during ammonization [27,28]. And the combination of oxidized coal with phosphate raw materials in the production of phosphate fertilizers leads to a significant degree of increase in the relative content of the assimilable form of P_2O_5 . When oxidized coal is added to the acidic superphosphate mass, humic acids, fulvic acids, and other organic acids, due to interaction with monocalcium phosphate and other phosphates, impede the process of retrograde, due to which the assimilable form of phosphorus does not decrease, but rather increases significantly upon ammonization of superphosphate mass.

According to modern agricultural requirements, it is desirable that in complex fertilizers the relative content of digestible forms of phosphorus compounds should be at least 50%. Therefore, for processing ordinary phosphate raw materials of the Central Kyzyl Kum, we consider the optimal norm of sulfuric acid to be 60% of the stoichiometric norm for the formation of monocalcium phosphate, and the weight ratio of phosphorite to oxidized coal (1: 0.25). In optimal conditions, when using the WCC, the fertilizer is obtained (weight. %): $P_2O_{5gen.}$ - 15.71; $P_2O_{5acq.}$ for citric acid - 10.45; $P_2O_{5acq.}$ Trilon B - 9.57; organic matter - 13.98; humic acids - 6.29; nitrogen - 1.97; $CaO_{gen.}$ -28.81; relative contents of $P_2O_{5acq.}$ for citric acid - 66.52 with a pellet strength of 2.1 MPa. And when using OPF, fertilizer is obtained (wt.%): $P_2O_{5gen.}$ - 10.62; $P_2O_{5acq.}$ for citric acid - 7.67; $P_2O_{5acq.}$ Trilon B - 6.63; organic substances - 10.46; humic acids - 4.71; nitrogen - 1.89; $CaO_{gen.}$ -29.06; relative contents of $P_2O_{5acq.}$ for citric acid - 72.22 with a pellet strength of 2.4 MPa.

Thus, the addition of oxidized coal with hydrogen peroxide to the superphosphate mass before ammonization and drying not only interferes with the retrograde process but also significantly increases the assimilable form of phosphorus and makes it possible to obtain effective humic superphosphate.

References

1. Roba, T.B. The Effect of Mixing Organic and Inorganic Fertilizer on Productivity and Soil Fertility // Open Access Library Journal, Pub. Date: June 26, 2018. doi: 10.4236/oalib.1104618.
2. Zhezhe N.G., Panteleeva E.I. Agrochemistry, Leningrad Publishing House Kolos, 1972, 288 pp.
3. Temirov Uktam, Namazov Shafolat, Reymov Akhmed, Usanbaev Najimuddin, Orakbaev Azamat. Animal waste processing technology and poultry farming in organomineral fertilizers // International Journal of Psychosocial Rehabilitation. Volume-24 Issue-06. – 2020. – pp. 7263-7274.
4. Eman A.A., Abd El-Monem, M.M.S. Saleh, E.A.M. Mostafa. Minimizing the quantity of mineral nitrogen fertilizers on grapevine by using humic acid, organic, and biofertilizers // Research Journal of Agriculture and Biological Sciences, 2008, 4(1): pp. 46-50.
5. Popov A.I. Humic substances properties, structure, formation. - Publishing House of St. Petersburg University, 2004.-248 p.
6. Orlov D.S. Humic substances in the biosphere. - M.: Nauka, 1993. - 19-30 p.
7. Abramets A. Aridgrow technology and humic preparations for greening arrangement of the arid, exhausted, and anthropogenic polluted territories // Khalifa international date palm award. - 2010. – N 3. – P. 44-45.
8. Filip Z., Bielek P., Demnerova K. Microbial Formation, Utilization, and Transformation of Humic Substances in Soil, Water, and Sediment //Int. Scientific Conf. «Humic Substances In Ecosystems 6». – Rackovadolina Slovakia, 2005. – P. 10-11.
9. Perminova I.V., Zhilin D.M. Humic substances in the context of green chemistry // Green chemistry in Russia. - M: Publishing house of Moscow State University, 2004, -146-162 p.
10. Golovkin G.S., Rode V.V., Maloletnev A.S., Lunin V.V. Coal - the raw material for the production of fuel and chemical-technological products // Chemistry of solid fuels. - Moscow, 2001. - No. 4. - 3-29 p.
11. Kuharenko T.A. On the definition and classification of humic acids // Chemistry of solid fuels. - Moscow, 1979. - No. 5. - 3 -11p.
12. Soboleva, E.V. Chemistry of combustible minerals. - M.: Publishing house of Moscow University, 2010. -237-239 p.
13. Dobrovolsky G.V., Nikitin E.D. Ecological functions of soils. M.: Publishing house of Moscow State University, 1986.- 12-24 p.

14. Orlov D.S. Soil humic acids and the general theory of humification. M.: Publishing House of Moscow State University, 1990. - P. 63 - 68.
15. Luo X.-S., Zhou D.-M., Liu X.-H., Wang Y.-J. Solid/solution partitioning and speciation of heavy metals in the contaminated agricultural soils around a copper mine in eastern Nanjing city, China // *Journal of Hazardous Materials*. 2006. Vol. A131. P. 19–27.
16. Chukov S.N., Golubkov M.S. A comparative study of the physiological activity of humic acids in soils on the algae culture *Chlorella vulgaris* // *Bulletin S. Petersburg State. un-t* 2005. No. 1. Ser. 3, pp. 103–113.
17. Magdi T. Abdelhamid, E.M. Selim, and A.M. EL-Ghamry, “Integrated Effects of Bio and Mineral Fertilizers and Humic Substances on 144 Growth, Yield and Nutrient Contents of Fertigated Cowpea (*Vigna unguiculata* L.) Grown on Sandy Soils”. *Journal of Agronomy*, 2011, № 10. C. 34-39.
18. Nardi S., Pizzeghello D., Muscolo A., Vianello A. Physiological effects of humic substances on higher plants // *Soil Biology & Biochemistry* 2002. V.34. P. 1527–1536.
19. Rose M.T., Patti A.F., Little K.R., Brown A.L., Jackson W.R, Cavagnaro T. R. Meta-Analysis and Review of Plant-Growth Response to Humic Substances: Practical Implications for Agriculture // *Advances in Agronomy*. 2014. V.124. P. 37-89.
20. Khristeva L.A. On the participation of humic acids and other organic substances in the nutrition of higher plants // *Soil Science*. - 1953, No. 10, - P. 46-59.
21. Khristeva L.A., Pivovarov L.R., Pshenichny A.E., Yarchuk I.I. On the relationship between the mineral and organic nutrition of higher plants and the use of humic acids as fertilizers // *Soil Science*. - 1954, No. 12, - P. 1-10.
22. Khristeva L.A. The physiological function of humic acid in the metabolism of higher plants // *Humic fertilizers. Theory and practice of their application. Part 1*. - Kharkov: Publishing house of Kharkov University, -1957, - P. 95-108.
23. Zherebtsov S. I., Malysenko N. V., Votolin K. S., Androkhonov V. A., Sokolov D. A. Humic preparations: Connection of structural and group composition and biological activity // *Bulletin of the Kuzbass state technical University*, 2018, no. 5, pp. 52-60.
24. Arinzhanov A.E., Miroshnikova E.P., Rebezo M.B. Prospects for the use of humic substances // *Electronic scientific and practical journal "Synergy"*, 2017. No. 1, p. 105-109.
25. Ganiev P.Kh., Namazov Sh.S., Beglov B.M. Usanbaev N.Kh. Oxidation of brown coal of the Angrenskoye deposit with hydrogen peroxide in an alkaline medium // *Universum: Engineering: electron scientific journal Moscow*, 2018. No. 9 (54). - P. 65-68.
26. Vinnik M.M., Erbanova L.N., Zaitsev P.M. Methods of analysis of phosphate raw materials, phosphorus and complex fertilizers, feed phosphates. M. : Chemistry, 1975. -- 218 p.
27. M.N. Nabiev, Vishnyakova A.A. Ammonized superphosphate from phosphorites of Karatau. Tashkent 1986.- 172 p.
28. Ganiyev P., Namazov Sh., Akhmedova I., Usanbayev N. Receiving Humic Plain Superphosphate based on the Private Phosphoric Meal of the Central Kyzylkum and the Oxidized Brown Coal of the Angren Field // *International Journal of Advanced Research in Science, Engineering and Technology* Vol. 6, Issue 4, April 2019