



ORGANOMINERAL FERTILIZERS BASED ON NITROGEN ACID PROCESSING OF ANGRENSK BROWN COAL AND PHOSPHORITES OF CENTRAL KYZYLKUM

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Abstract

The article presents the results of a study of the process of obtaining organomineral fertilizers by oxidation of Angren brown coal with nitric acid and subsequent decomposition by oxidation products of ordinary phosphorite flour, dust-like fraction, thermally and chemically enriched concentrates of phosphorites of the Central Kyzyl Kum. From all types of raw materials, even such poor ones as ordinary phosphate flour and pulverized fraction, highly effective nitrogen-phosphorus-humic fertilizers are obtained.

In our previous work [1], it was shown that such acute problems of agricultural production in the Central Asian region as a lack of mineral fertilizers, a decrease in the humus content in the soil and soil salinization, can to some extent be solved by organizing large-scale production and using organic mineral fertilizers from brown coal. But brown coal must contain at least 45% of humic acids [2]. Such raw materials can be obtained by oxidizing coal with nitric acid.

The possibility of obtaining organomineral fertilizers based on the oxidation of coal with nitric acid has long been of interest to scientists. Thus, in [3], the optimal conditions for the reaction of lignite with dilute nitric acid were studied. The yield of nitrohumic acids, the amount of unreacted HNO_3 , and the yield of valuable by-products were determined. From 100 parts of dry ashless lignite at 80°C , 84 parts of an organic solid insoluble in water were obtained, 92% of which was dissolved in cold dilute alkali. In the work [4], it was reported that the Research Council of Alberta started up a semi-plant with a capacity of 180 tons/year to obtain slow-acting nitrogen fertilizer from bituminous coal and lignite. Powdered coal was treated with ammonia, and ammoniated coal - with nitric acid and ammonia water. The product contained 20-22% N, of which one third (in the form of ammonium salts) in a rapidly assimilable form, the rest in a slowly assimilated form. The high agrochemical efficiency of the fertilizer is noted. The article [5] presents the results of studies of the oxidation of brown coal with nitric acid to obtain organomineral fertilizers. The optimal dose and concentration of HNO_3 and the composition of the evolved gases have been determined. A scheme for the production of fertilizers with full utilization of released nitrogen oxides is given. Under the optimal mode of oxidation of brown coal, the yield





of humic acids is 1 kg/kg of nitric acid monohydrate. In [6], nitrohumic preparations were obtained by treating brown coal with a mixture of nitric and sulfuric acids, and then with ammonia water. Tests under hydroponic conditions have shown their stimulating effect on plant growth.

According to the patent [7], fertilizer from brown coal is obtained by pretreating it with nitric acid and subsequent neutralization of the reaction product at a temperature of 20 - 120 degrees Celsius in the presence of water. According to the Australian patent [8] for the production of slow-dissolving nitrogen fertilizer, 13.5 kg of low-calorie brown coal in finely divided form are mixed with 4.1 kg of carbamide powder. After that, 337 g of concentrated nitric acid are added to the mixture, then 84 g of NaOH, dissolved in a small amount of water. The mixture is then injected with 14 kg of ammonia water with a specific gravity of 0.880 g/cm³. The gel is dried and used as fertilizer. In [9], the process of obtaining fertilizer is similar to that described in [8] with the only difference that in the first case, alkali NaOH, KOH and NH₄OH are added after nitric acid, in the second - before the oxidizing agent.

According to [10], the method for obtaining a complex organo-mineral fertilizer is as follows: 1 kg of dry ground brown coal is oxidized with 2 liters of nitric acid with a specific gravity of 1.2 - 1.4 g / cm³ at 60 ° C for 5 hours. A diluted alkali solution is added to the oxidized product at the rate of 5 liters of normal NaOH solution per 1 kg of brown coal to maximize the extraction of oxidation products. Iron or manganese carbonates are added to the resulting mixture when heated to 60 ° C until the reaction is completed. The resulting solution containing fertilizer is separated from the solid phase by decantation. It can be stored for several years. To obtain a dry fertilizer, the solution is evaporated at 40 - 80 ° C. A dry powder is obtained that dissolves well in water without changing its chemical and biological properties. Due to the fact that the obtained fertilizers contain a mixture of iron and manganese metals with products of oxidative and thermal destruction of brown coal, they are characterized by high stability in an alkaline and acidic environment, which allows them to be used on any soil at a consumption of 5-10 kg/ha.

In [11], the possibility of obtaining fertilizers based on two-stage nitric acid oxidation of brown coal (lignite) containing 20% humic acids was established. In the first stage, the coal is oxidized to nitrohumic acid with dilute (6N) nitric acid at 85 ° C for 45 minutes. with a mass ratio of nitric acid to incoming coal equal to 8. In the second stage, the obtained nitrohumic acid is oxidized for 30 min with more concentrated nitric acid (14 N) at 50 ° C and a HNO₃: carbon ratio equal to 10. The oxidized water and acid-soluble product is ammoniated at 80 ° C. 30 minutes; mass ratio NH₃: coal = 10. The product contains 15% N, has a high-water retention capacity, aggregates the





soil and supplies it with carbon. In [12], lignite samples were oxidized with 20% nitric acid at 75 ° C and then treated with ammonia in a fluidized bed reactor at a temperature of 100-375 ° C for 2 hours. The total nitrogen content in the product increased with increasing temperature and amounted to 7-13%. The maximum rate of nitrification in the soil was achieved when using the product obtained at an ammonization temperature of 100 ° C. And the degree of conversion of nitrogen into nitrates was 45% for the resulting fertilizer.

But it is most advisable to combine brown coal oxidized with nitric acid with phosphorus fertilizers and phosphate raw materials, since it reduces the retrogradation of phosphorus in the soil, increases the efficiency of phosphorus for plants and converts the indigestible form of phosphorus in raw materials into a form assimilable for plants [13]. In the works listed below, just such a combination is implemented. In [14], granular complex fertilizer is obtained by mixing crushed rock of coal mines or coal preparation plants with superphosphate in a weight ratio of 11:1, and then the mixture is treated with nitric acid with a density of 1.12 - 1.13 g/cm³ in an amount of 16 - 20% to weight of dry components with subsequent neutralization of the resulting mass with ammonia water.

In [15], complex organomineral fertilizers with a total P₂O₅ content of 14–20%, including assimilable 9–15, water-soluble 8–12, total nitrogen 15–20% and organic carbon 10–15%, with free acidity 0.5 - 5% is obtained by decomposition of phosphate raw materials with 45 - 55% nitric acid in the presence of ammonium nitrate or carbamide with the addition of brown coal. The process is carried out at a temperature of 30-800C for 5-120 minutes. The resulting pulp is neutralized with ammonia and sent to a screw granulator, where recycle is fed in an amount of 2-10 wt. h. for 1 wt.h. pulp. Then the material enters the drying drum, where it is dried with direct-flow flue gases at a temperature of 2000C, then it is cooled in the drum and enters the classification.

In works [16, 17], the possibility of using brown humic coal from the Kzyl-Kiya deposit (Kyrgyzstan) for processing nitric acid extract of phosphorites of Karatau (Kazakhstan) for organic fertilizer was investigated. The norm of nitric acid for the decomposition of phosphate rock was 103%. It was found that an increase in the acidity of the extract prevents the extraction of humic acids from coal. The process of P₂O₅ retrogradation during the ammonization of the extract is inhibited due to the formation of calcium humates. The rate of humic coal significantly affects the content of the water-soluble form of P₂O₅ and the physicochemical properties of the resulting fertilizer. Carrying out the process of ammonization of the extract in the presence of brown coal sequentially in two stages at an optimal temperature of 50°C, a product



can be obtained with a content of 96-98% of digestible and 45-48% of water-soluble forms of P_2O_5 .

The work [18] is closest to our problem. In it, raw brown coal was processed with 5 N. nitric acid. Oxidized coal samples were mixed with ground phosphorite, aqueous ammonia, and urea. Oxidation of coal has led to a decrease in its carbon content. The hydrogen content changed slightly. The content of organically bound nitrogen increased from 1% in the starting material to 11-13% in fertilizers. The amount of humic acids and fulvic acids in coal has significantly increased. From the added phosphorite, due to the residual nitric acid and the formed organic acids, part of the phosphorus passed into the form assimilable for plants. In short-term growing experiments, even with the introduction of high amounts (2 t/ha), no phytotoxic effect was observed.

We have set ourselves the goal of creating complex organomineral fertilizers based on brown coal from the Angren deposit and phosphorites of the Central Kyzylkum desert by treating them with nitric acid. A representative sample of small coal fines of the BNSSSH brand (brown, nut, small, seeds, shtyb) was used in the work, having, after drying to an air dry state and grinding in a ball mill to a particle size of 0.25 mm, the following composition (weight %): moisture 14.1; ash 13.7; organic 72.2; humic acids 4.1% for organic matter. Nitric acid was taken from Chirchik JSC "Electrokhimprom" with a concentration of 59%. Samples of phosphate raw materials were taken by us from the Kyzylkum phosphorite plant. A chemically enriched concentrate was obtained by us [19, 20]. The composition of the starting phosphate raw material is given in table. 1.

Table 1. Composition (weight %) of the starting phosphate raw material.

Types of phosphorites	P_2O_5	CaO	Al_2O_3	Fe_2O_3	MgO	F	CO_2	$\frac{CaO}{P_2O_5}$
Ordinary phosphate rock	18,8	46,71	1,24	1,05	1,75	2,0	15,19	2,48
Dust fraction	18,54	44,72	0,95	0,80	0,80	2,22	14,80	2,41
Thermoconcentrate	27,26	53,36	1,30	0,51	0,61	2,91	2,41	1,96
Chemically enriched концентрат	26,86	46,54	0,35	0,55	0,61	3,12	6,20	1,73



The experiments were carried out as follows. A 30% aqueous solution of nitric acid was poured into a glass reactor with a helical stirrer and a thermostating water jacket. After heating to 40°C, a stirrer was switched on and a sample of coal was gradually fed. The weight ratio of the organic part of the coal to the monohydrate of nitric acid was taken 1: 1.6 and 1: 2.0. Coal oxidation was carried out for 75 min. The resulting oxidation product was used to treat phosphate raw materials. The amount of phosphorites was calculated based on the amount of nitric acid initially taken for the oxidation of coal. The rate of this acid for the decomposition of phosphorites was taken by us in the amount of 40-80% of the stoichiometry for calcium oxide in the raw material.

The decomposition of phosphorite was carried out at a temperature of 40°C for one hour. Then the mass was ammoniated to a pH of 3.7-4.2, dried at 70-75°C to a moisture content in the product of 4-6% and analyzed. The analysis was carried out according to well-known methods [21, 22]. The assimilable form of P₂O₅ in the product was determined both by 2% citric acid and by 0.2 molar solution of Trilon B. The experimental results are shown in table 2.

Thus, nitric acid processing of brown coal from the Angren deposit and phosphorites of the Central Kyzyl Kum, even such poor ones as ordinary phosphate rock and pulverized fraction, makes it possible to obtain highly efficient nitrogen-phosphorus-humic fertilizers from them.

References

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