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PHOSPHATE ROCK: METHODS OF PREPARING AND APPLICATION

The results of research for improving physical-chemical and agrochemical properties of phosphate flour, obtained by phosphate various deposits enrichment, by increasing its grinding fineness, as well as mechanical activation in the presence of various physiologically active substances, also through its partial activation incomplete stoichiometry norm of the hydrochloric and nitric acids are represented.

Introduction. The main raw materials for the production of phosphate fertilizers are natural phosphorite and apatite ores, differing not only in mineralogical composition, conditions of formation, but also technological properties. Ascertained phosphate ore reserves are accounted for more than 60 countries and currently estimated at 63 067 million tons P_2O_5 , including 57 807 million tons of phosphate (91 wt. %) and 5.26 million tons of apatite (9 wt. %) ores [1–3].

The situation analysis in the global market of phosphate raw materials allows revealing the following adverse trends that will only grow and have a significant impact on producers and consumers of phosphate fertilizers:

– Export decline in phosphate raw materials by its traditional suppliers and increase in the proportion of phosphate raw materials processed by local producers of phosphate fertilizers;

– Deterioration of phosphate raw material quality as a result of depletion of high-quality ores;

– The emergence of an imbalance between supply and demand by reducing the growth rate of extraction of phosphate raw materials while increasing the demand for phosphate fertilizers.

These trends make it necessary to search and use alternative sources of phosphate raw materials.

Main part. Phosphate fertilizers are divided into three main groups according to the degree of solubility: water-soluble – ammoniated superphosphate, double superphosphate, ammophos, diamphos; not soluble in water, but citrate- and lemonsoluble – precipitate Thomas slag, Martin phosphate slag, thermal phosphates; sparingly soluble phosphates – phosphate rock. Phosphate rock was the first phosphorus fertilizer, widely used in different agro-climatic regions. Its industrial output in Russia was initiated thanks to the works of A.N. Engelgrad. This is due to several factors, the most important of which are:

– A unit of P_2O_5 in phosphate rock is 2–4 times cheaper than in any water-soluble phosphate fertilizers;

– Production of phosphate rock eliminates the production of large-tonnage environmentally hazardous waste;

– Phosphate fertilizer is made from the most affordable phosphate raw material – phosphate rock;

– Phosphate rock as opposed to water-soluble fertilizers is slowly soluble one with a long lifespan.

In addition, phosphate rock is produced by simple technology without formation of burdensome large-tonnage production wastes such as phosphogypsum.

Production of phosphate fertilizer includes preliminary coarse crushing of clean ore on hammer or jaw crushers, drying with flue gases in rotary dryers, subsequent secondary crushing and dry grinding. Secondary crushing is done on the roller or hammer mills. For fine grinding ball or air-jet mills are used. The separation of finished phosphate fertilizer from the larger particles to be returned to the regrinding is carried out in an air separator [4].

At present, the utilization of nutrients of applied fertilizers is insufficient and ranges between 20–60 wt. %. Unlike nitrogen and potassium which losses are mainly due to the leaching with ground- and rain waters, low utilization of phosphorus (18–25 wt. % per year) is caused by its immobilization in the soil or P_2O_5 retrogradation, which is determined primarily by soil acidity and by content of free aluminum and iron ions in it, as well as active sesquioxides.

Aluminosilicate and iron phosphates are sparingly soluble in water compounds. Their formation begins immediately after application in soil high-concentration water-soluble phosphate fertilizers. Most crops (cereals, potatoes, sugar beets) assimilate phosphorus with a maximum speed only 2–4 months after sowing. By this time most of concentrated water-soluble fertilizers such as ammophos change on the acidic soils into marginally soluble compounds of iron and aluminum and concerning agrochemical efficiency their effect on crop yields is close to the action of phosphate fertilizer.

The Mstislavl field is the most promising according to conditions for the occurrence and extraction of phosphate rock. Mstislavl phosphorite ore refers to the subtype of poor ores with low iron content of nodular type with P_2O_5 content from 8 to 15 wt. %.

Extensive researches on washability of phosphate ores from Mstislavl deposits carried out over a number of years showed that Belarusian phosphates are finely disseminated ores difficult for concentration. It is established that as a result of the primary concentration conducted by a dry or wet ore crushing, separation by size pieces on screens and by waste rock washing with water, P_2O_5 content in the concentrate increases to 15–16 wt. %. Then the concentrates of primary enrichment are exposed to deeper secondary concentration by flotation. In the circle of basic flotation the concentrate was obtained containing 20–22 wt. % of P_2O_5 , and after three recleanings P_2O_5 content in the finished product increases to 27–28 wt. % at recovery of 80–90 wt. %, that can be used in the preparation of compound fertilizers.

The resulting products, both in the first and second concentration contain indigestible for plants form P_2O_5 . Transforming them into mineral phosphate fertilizers is their transitions from an indigestible P_2O_5 form into digestible. Nowadays many ways to activate and to upgrade them have been proposed. This is usually done by decomposition of phosphate raw materials with mineral acids: sulfuric, nitric, phosphoric and hydrochloric acid. But for the acid treatment high-quality phosphate rock is required. This process is complicated, labor and energy intensive and is accompanied by the formation of large waste amounts, in particular phosphogypsum which disposal is now a big problem.

It was studied the impact of mechanochemical activation on the phosphate rock to increase its component dilution, it was investigated the effect of physiologically acidic additives (eg, ammonium sulfate) on the mechanochemical activation process, the kinetic parameters of the process, including the content of water- and citrate soluble phosphate salts depending on the activation conditions, the type and the ratio of physiologically acid additives etc were determined. (Table 1).

A number of factors on the activation of phosphate rock of various fineness in the presence of adjuvants were studied Ammonium sulfate, ammonium chloride and potassium and mixtures thereof were used as suitable physiologically acidic additives. The concentrate obtained at the first enrichment (P_2O_5 content of 15.6 and 16.2 wt. %) from Mstislavl phosphate rock deposits and Polpinski phosphorite rock field (P_2O_5 – 18.9 wt. %) were used as a phosphate raw material.

Table 1

Effect of activation duration and physiologically acidic additives on the content of lemon soluble P_2O_5 form (fraction –0.063 mm) phosphorite rock from Mstislavl field (P_2O_5 total content – 16.25 wt. %)

Fertilizer composition	Time min	Composition wt. %		P_2O_{5LS}/P_2O_{5total} , %
		P_2O_{5total}	P_2O_{5LS}	
Ammonium sulfate : phosphate rock = 1 : 1	5	9.08	7.63	84.0
Ammonium sulfate : phosphate rock : potassium chloride = 1 : 1 : 1	5	7.73	7.00	90.6
Ammonium sulfate : phosphate rock R = 1 : 1	10	9.08	7.75	85.4
Ammonium sulfate : phosphate rock : potassium chloride = 1 : 1 : 1	10	7.73	7.04	91.07
Ammonium sulfate : phosphate rock = 1 : 1	15	9.08	7.94	87.5
phosphate rock: potassium chloride = 1 : 1	15	12.95	8.59	66.3
Ammonium sulfate : phosphate rock potassium chloride = 1 : 1 : 1	15	7.73	7.44	96.25
Ammonium sulfate : phosphate rock = 1 : 1	30	9.08	7.92	87.2
phosphate rock : potassium chloride = 1 : 1	30	12.95	8.59	66.4
Ammonium sulfate : phosphate rock : potassium chloride = 1 : 1 : 1	30	7.73	7.43	96.1

The above data clearly show that the interaction of physiologically acidic additive agents with phosphate rock, or rather with its phosphate component, the activation of the latter occurs, which promotes the transfer of phosphorus compounds into a more mobile form, as evidenced by a significant increase in the relative content of P_2O_5 lemon soluble form. Increasing the mixing time leads to the rise of the phosphate fertilizer activation in the presence of only ammonium sulfate or potassium chloride, and at their combined introduction, the maximum value is attained at 15 min interaction. Further experiments were conducted at the activation time 15 min.

Activation of phosphate rock under the influence of nitrogenous fertilizers, particularly ammonium sulphate is considerably more effective than when exposed to potassium chloride, which can be attributed to the higher acidity of ammonium

sulphate in comparison with potassium chloride (Table 2). The content of digestible P_2O_5 form in relationship to the total P_2O_5 when activated with ammonium sulfate at a ratio of $N : P_2O_5 = 1 : 1$ reaches up to 87.5 wt. against 66.3% wt. % with potassium chloride at the same ratio of components and the same time of activation. The most phosphate activation is observed in the ternary systems. In this case the synergism of activating effect becomes apparent. Combined nitrogen and potassium fertilizer introduction activates phosphate fertilizers much more significantly on the basis of phosphorite rock than each individually

Table 2
Influence of the composition, the ratio of components in the mixture, the grind size on the activation of washed phosphorite concentrate from Mstislavl deposit (P_2O_{5total} content – 15.6 wt. %, the mixing time 15 min)

Fertilizer composition	Size, mm	content in the mixture, wt. %		$\frac{P_2O_{5LPS}}{P_2O_{5total}}$ %
		P_2O_{5total}	P_2O_{5LSP}	
Ammonium sulphate : phosphate rock = 1 : 1	-0.16	8.58	7.25	84.5
phosphate rock : potassium chloride = 1 : 1	-0.16	12.24	6.13	50.0
Ammonium sulphate : phosphate rock : potassium chloride = 1 : 1 : 1	-0.16	7.43	6.75	90.8
phosphate rock : potassium chloride = 1 : 2	-0.16	6.30	5.75	91.3
phosphate rock : potassium chloride = 1 : 2	-0.16	10.60	7.63	72.2
phosphate rock : potassium chloride = 1 : 1	-0.063	8.58	8.00	93.2
phosphate rock : potassium chloride = 1 : 1	-0.063	12.24	8.50	69.4
Ammonium sulphate : phosphate rock : potassium chloride = 1 : 1 : 1	-0.063	7.43	7.00	94.5
phosphate rock : potassium chloride = 1 : 2	-0.063	6.30	6.25	99.2
phosphate rock : potassium chloride = 1 : 2	-0.063	10.60	8.13	76.6

Furthermore, in all cases studied the content of lemon soluble P_2O_5 form both in absolute and in relative expression significantly increases with the rising dispersion of phosphorite rock. Thus, if at

activation of washed phosphorite concentrate with overall size 0.16 mm in a binary mixture with ammonium sulfate or potassium chloride at a ratio of $N : P_2O_5$ and $P_2O_5 : K_2O = 1 : 1$ or $N : P_2O_5 : K_2O = 1 : 1 : 1$ the content of lemon soluble P_2O_5 form is 7.25, 6.13, 6.75 wt. % respectively, so in the case of activation of the fraction -0.063 mm – 8.00, 8.50, and 7.00 wt. % respectively. Relative digestibility of fine fraction phosphorus at activation with ammonium sulfate, potassium chloride, or a mixture thereof is 93.2, 69.4 and 94.5 wt. % vs. 84.5, 50.0 and 90.8 wt. % respectively, for a fraction of size 0.16 mm (Table 2).

From these data it follows that in this case i.e. at activation fine fraction rock -0.063 mm obtained when grinding the initial ore of total coarseness -0.16 mm, the fine-dispersed milling of phosphorite concentrate is at the chemical activation advantages. Elevated levels of ammonium sulphate and potassium chloride enhance phosphorite rock activation.

Thus, if at the ratio $P : N$ and $P : K = 1 : 1$ the relative solubility is 84.5 and 50.0 wt. % respectively, then at the ratio of 1 : 2, this figure has risen to 91.3 and 72.2 wt. % respectively (the fraction -0.16 mm). For samples of $P : N$ and $P : K = 1 : 2$ (-0.063 mm fraction) relative digestibility increased up to 99.2 and 76.6 wt. vs. 93.2% and 69.4 wt. % respectively, at a component ratio of 1 : 1.

Similar activation results were obtained when used as a phosphorite component in NPK-phosphate fertilizers from Polpinski field.

Thus, it was found that pre-mixing of ground phosphate rock with physiological acidic additives can be regarded as one of the methods of improving the effectiveness of phosphate rock. This is confirmed by agrochemical tests of mixtures of ground phosphate rock from Mstislavl phosphate deposits with ammonium sulfate. It is shown that its effectiveness both on sod-podzol loamy and on sandy soils increases to the level of the best forms of phosphorus water-soluble fertilizers (ammophos and ammoniated superphosphate).

Another unconventional method of obtaining phosphate fertilizers from poor phosphate raw material is its treatment with inorganic acids, but in much smaller quantities than it is required for the complete decomposition of phosphate rock. In this case the so-called under- or partial decomposition of phosphates are formed.

Agrochemical phosphate fertilizer efficiency, untreated and treated with acids, was compared with that of water-soluble phosphates. The interaction of water soluble phosphate with the soil reduces its availability to plants while the treated with small amounts of acids phosphorite under these conditions, becomes both absolutely and relatively more effective.

Table 3

**The chemical composition of the ground phosphate rock,
obtained by concentration of phosphates from Polpinski field**

P ₂ O ₅	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	F	SO ₃	H ₂ O	H.o.	P.p.p
18.9	29.4	0.63	2.29	1.61	3.36	2.5	2.3	1.05	0.55	7.51

The best results were obtained with embodiments of phosphoric acid; the effectiveness of the products of incomplete decomposition of phosphate rock with hydrochloric and nitric acids was lower. Harvest of some embodiments of experience as a result of the phosphorite activation increased more than twice compared with the harvest assisted by the untreated phosphate rock. The optimal dose of phosphoric acid for treatment is 7.8 wt. % from weight of phosphate rock. When phosphate rock processing with phosphoric acid it has been additionally absorbed from it almost two times more phosphorus than from not processed phosphate rock. Thus the efficiency of the agent used for the partial decomposition is 5–8 times higher than for soluble phosphate.

In order to process the optimal composition of complex fertilizers, in which a portion (10–30 wt. %) of water-soluble phosphates such as ammophos will be replaced by a cheaper and affordable chemically activated phosphorite, we have conducted the researches on activation of nodular phosphorites from Polpinski deposits with hydrochloric and nitric acids taken in the lower quantity than it is necessary according to the stoichiometric standard. The concentration of nitric acid was 55.7 wt. %, hydrochloric – 21.8 wt. %. The chemical composition of the investigated phosphate rock is presented in Table 3.

Phosphorite concentrate from Polpinski deposits is received after the initial ore concentration by washing, followed by primary flotation. The chemical and X-ray analysis results showed that the main rock-forming phosphate mineral in the studied samples is fluorinecarbonateapatite.

The studies found that modifying acids influence simultaneously all the components of the phosphate fertilizer on the particle surface. They contribute to the degradation of impurity minerals and to the formation of water-soluble and lemon-soluble phosphates. With increasing modifying acid content, the calcium and iron ion extraction into aqueous and into 2% citric acid phosphate extract increases as well.

Hydrochloric acid is a more potent activator of the phosphate fertilizer than nitric acid: data on component extraction into the aqueous extract and into 2% citric acid sample extract modified with hydrochloric acid is higher than with the nitrogen acid. It is shown that with increasing modifying acid content the degree of all component extraction increases as well. The extraction degree value into

the aqueous extract Ca (from 12.1 to 37.97 wt. % (treatment HCl) and from 6.59 to 29.02 wt. % (treatment HNO₃)) is higher than the recovery rate of P₂O₅ (from 2, 9.88 to 66 wt. % (treatment HCl) and from 1.72 to 14.3 wt. % (treatment HNO₃)). This difference means that the acids affect on impurity minerals to a greater degree than on the basic phosphate substance.

It is shown that the following P₂O₅ composition relations: inorganic acid: with hydrochloric acid treatment of P₂O₅ : HCl = 1 : 0.2, with nitric acid treatment P₂O₅ : HNO₃ = 1 : 0.4 can be considered as optimal conditions to improve the quality characteristics of phosphate rock.

Conclusion. It was established that in the presence of physiologically acidic additives, phosphate rock is activated, as evidenced by a significant increase in the relative lemon soluble form of P₂O₅ composition.

It is shown that activation of phosphate rock under the ammonium sulfate influence occurs more efficiently than in the presence of potassium chloride that due to the higher ammonium sulfate acidity compared to the potassium chloride.

It is shown that in the presence of physiologically acidic substances, numerous defects in the crystal lattices of phosphate rock phosphate minerals are formed. Their profound transformation, phase transformations with possible partial substitution of calcium cations with potassium and ammonium cations, and fluorine anions with hydroxyl – and chlorine ions occur within the fluorinecarbonateapatite structure.

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