Cyclic Technology for Obtaining Double, Triple Superphosphate and Concentrated Nitrogen-Phosphorus Fertilizer from Low-Grade Phosphorites of Central Kyzylkum

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ABSTRACT

This article presents data from studies on the processing of low-grade phosphorites into unilateral and complex phosphorus fertilizers in a cyclic way. Based on the neutralization of acidic products of monocalcium phosphate isolated from the crystallization process, off-balance ore and limestone, double and triple superphosphates were obtained with a content of: $P_2O_{5tot.}$ from 44.43 to 47.09%; $P_2O_{5usv.} : P_2O_{5tot.} = 94.24$-97.86% and P_2O_5tot. from 50.05 to 53.38%; $P_2O_{5usv.} : P_2O_{5tot.} = 97.08$-99.59%, respectively. And by neutralizing acid monocalcium phosphate with ammonia to pH = 4.5-4.8, NP-fertilizers were obtained with the content (wt.%): N from 8.97 to 10.12; P_2O_5 tot. from 55.18 to 56.64 with relative water form P_2O_5 aq. from 79.85 to 85.91%.

Introduction

Phosphorites of the Central Kyzyl Kum belong to phosphorus-poor ores (≤17% P_2O_5) with a high content of carbonate minerals (≥16% CO_2), which exceeds the limit of the calcium modulus, i.e. CaO/ P_2O_5 = 2.7 versus 1.5 [1,4,5].
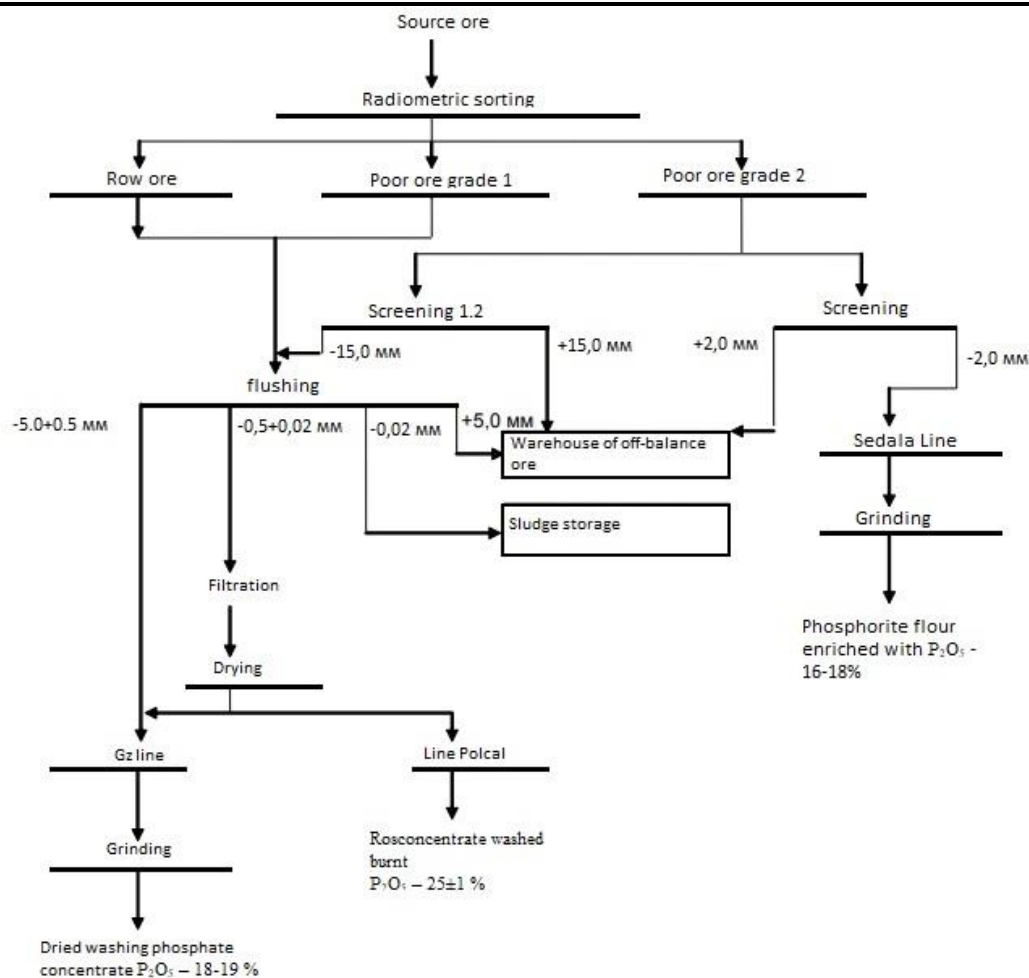
The main part

From practice, it is known that phosphate rock with a high carbonate content is subjected to thermal roasting (680-980°C) with subsequent leaching of free calcium oxide from it with water or salt solutions (seawater can be used)

[2,3]. In order to meet the needs of agriculture of the Republic of Uzbekistan for phosphate fertilizers, which is 688.4 thousand tons of 100% P_2O_5, the Kyzylkum Phosphorite Complex (KPC) from 2007 to 2014 increased the production capacity of washed calcined concentrate (MOC) from 400 thousand .t up to 716 thousand tons per year with an average P_2O_5 content of at least 26% (Fig. 1.). However, the currently functioning technological scheme of enrichment at KFK cannot be considered rational, because the increase in the concentration of P_2O_5 in the MOC (26% P_2O_5) is

only 8.42% compared to its concentration in the original ore (17, 58%) occurs against the background of a significant loss of P_2O_5 with enrichment tailings with the status of "off-balance ore" (134.77 thousand tons of P_2O_5 or 42% of the original P_2O_5 in the ore). To date, more than 13 million tons of mineralized mass and more than 5 million tons of slurry phosphorite have already been accumulated. [6,7,8]. However, the amount of phosphate fertilizer produced in the amount of 138 thousand tons of P_2O_5 is far from the needs of agriculture (688.4 thousand tons). And the produced phosphate fertilizers are complex, which make up about 80% of the produced phosphate fertilizers. Agrochemists have found that phosphate fertilizers give the greatest effect when they are applied under autumn plowing. For cotton, 60% of phosphorus must be applied for fallow, and for grain crops - all 100% of phosphorus. Therefore, it is extremely important to provide agriculture with a single phosphorus fertilizer [9,10,11,12,13,14]. However, for the production of one-sided fertilizers of double superphosphate by the traditional chamber, chamber-flow, flow and return (Dorr-Oliver) methods, condensed raw materials (at least 32% P_2O_5) are required, which are not produced in the republic. In addition, all of these methods are obsolete (chamber, chamber-flow), low productivity (flow), high costs for the fractionation process, mechanization and low productivity (Dorr-Oliver method), due to high return, i.e. 15 per 1 ton of finished product. [15,16,17,18]. all of these methods are obsolete (chamber, chamber-flow), low productivity (flow), high costs for the fractionation process, mechanization and low productivity (Dorr-Oliver method), due to high return, i.e. 15 per 1 ton of finished product. [15,16,17,18]. all of these methods are obsolete (chamber, chamber-flow), low productivity (flow), high costs for the fractionation process, mechanization and low productivity (Dorr-Oliver method), due to high return, i.e. 15 per 1 ton of finished product. [15,16,17,18].

Rice. 1. Technological scheme of production at KFK.

Based on the foregoing, this article studies the process of obtaining single phosphate fertilizers - double and triple superphosphate, and as a complex fertilizer - a highly concentrated nitrogen-phosphorus (NP) fertilizer in a cyclic way. Object and methods of research. To research the production of double, triple superphosphates and NP-fertilizers used high-carbonate phosphorites of the Central Committee - ordinary phosphorite flour (RPM: 17.37% P_2O_5, 47.13% CaO, 14.89% CO_2), mineralized mass (MM: 14.33% P_2O_5, 43.66% CaO, 14.70% CO_2), MOC: 25.77% P_2O_5, 52.70% CaO, 3.60% CO_2, as well as concentrated extractive phosphoric acid (EPA), obtained by the dihydrate method from the MOC of phosphorites of the Central Committee of the following composition (wt.%): 41.20 P_2O_5; 0.20 CaO; 0.98 MgO; 0.79 $Fe2O3$; 1.76 $Al2O3$; 3.33SO3; 1.05F

Before obtaining phosphorus fertilizers, studies were carried out to determine the thermodynamic constants of the decomposition process of RPM and MOC of concentrated EPA. The study of the decomposition kinetics of RPM and MOF was carried out at temperatures of 70, 80, 90, and 100°C, corresponding to 343, 353, 363, and 373 K on the Kelvin scale (T=273+t). ICF with a process duration of 5; ten; fifteen; thirty; 60; 90 and 120 min. After a predetermined time, the contents in the reactor were filtered on a heated Buchner funnel with a constant vacuum of 150 mm Hg. (0.2 atm.). The washed precipitate was dried at 100–105°C and then analyzed for the content of P_2O_5tot. and P_2O_5aq.. according to the procedure. Taking into account the crystallization field of the ICF based on the above-studied influencing factors, the IOC phosphate mineral opens up within 74, 98-81.79% at a rate of 300-400% for EPA

41.20% P_2O_5. In the case of RFM Kraz. reaches the range of 94.43-97.61% at a rate of 400-500% for EPA 41.20% P_2O_5. This indicates that the MCF crystallization field is mainly formed between the boundaries of the kinetic and diffusion regions. Experimental data on Kraz values. allowed to calculate the decomposition rate constant according to the first-order equation:

(one)
$$K = 2{,}303 / \tau \cdot \lg C / (C_0 - C_\tau)$$

Formula (1) can be represented as:

$$K = 2{,}303 / \tau \cdot \ln\left(1 / (1 - K_{pa3.})\right) \quad (2)$$

The decomposition rate constant of MOF and RFM depending on the temperature also obeys the Arrhenius equation and differs from each other only by different absolute values. Based on the established values of the reaction rate constants for the decomposition of the phosphate concentrate, the apparent activation energy (Ea) was determined.

Results and its discussion. Depending on the rate of stripped off phosphoric acid at temperatures of 343-373 K, the value of the apparent activation energy Ea of the MOF and RFM lies from 2.23 to 2.92 kcal/mol or from 9.33 to 12.23 kJ/mol and from 2.11 up to 3.72 kcal/mol or from 8.85 to 15.59 kJ/mol, respectively. Activation energy indicators indicate sufficient reactivity of phosphorite phosphorites of the Central Committee during its phosphoric acid processing, regardless of the norm, EPA concentration and temperature. Judging by the results of the experiment, the more optimal norm for the concentration of EPA 41.20% P_2O_5 is 350 and 450%, respectively, for the decomposition of RFM and MOF. Further studies were carried out to obtain double and triple superphosphate. Laboratory experiments were carried out under thermostatic conditions using a tubular glass reactor equipped with a screw stirrer with an electric motor. The study was carried out at 95°C for 60 min. After separating the pulp into an under decomposed phosphate precipitate, a saturated solution of monocalcium phosphate (MCP) was separated into a solid and liquid phase. Crystallized acid MCF was subjected to neutralization according

to the equation: $Ca(H_2PO_4)2 + 2H_3PO_4 + CaCO_3 = 2Ca(H_2PO_4)2 + H_2O + CO_2$

$Ca(H_2PO_4)2 + 7H_3PO_4 + Ca5(PO_4)3F = 6Ca(H_2PO_4)2 + HF$
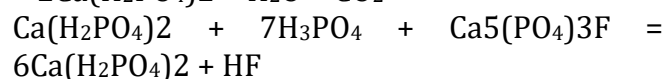
The rate of phosphate raw materials was taken to neutralize free H_3PO_4 within 70–100% of the stoichiometry for the formation of $Ca(H_2PO_4)2$. The process of acid MCF neutralization was carried out at 75–80ºC for 30 min, followed by granulation by pelletizing. Then the obtained granules were dried at 90-95°C. In this case, the pH of the final products is at least 3.0, they contain P_2O_5free. fluctuates between 1.15-3.0%.

Under optimal conditions of MOF (NEPA - 350% and SEPA - 41.20% P_2O_5) with the use of a neutralizing additive -MM, the following product (wt.%) was obtained: P_2O_5tot. from 44.43 to 47.09%; P_2O_5usv. according to lim. to-those: P_2O_5 tot. = 94.24-97.86%; P_2O_5 usv. tril. B: P_2O_5tot. = 91.45-94.75%; P_2O_5aq. : P_2O_5 tot. = 83.46-90.83%. In terms of composition and quality, they meet the requirements of GOST 16306-80 for double superphosphate grade "B". When using ground natural limestone (54.45% CaO and 43% CO_2), the finished product with the content of P_2O_5tot. from 50.05 to 53.38%; P_2O_5usv. : P_2O_5 tot. = 97.08-99.59%; P_2O_5 aq. : P_2O_5tot. = 84.04-90.18%. In terms of composition, these fertilizers can be attributed to double superphosphate grade "A" (GOST 16306-80) or triple superphosphate, and they are export-oriented products.

The process of obtaining NP-fertilizers was carried out by ammonization (up to pH = 4.5-4.8) of acid MCF was carried out using 25% ammonia water. Depending on the conditions of the experiments, the composition of the finished nitrogen-phosphorus fertilizers varies (wt%): N from 8.97 to 10.12; P_2O_5tot. from 55.18 to 56.64; P_2O_5 usv. from 53.89 to 56.57; P_2O_5aq. from 44.06 to 48.66. The relative contents of digestible and aqueous forms of P_2O_5 are, respectively, from 97.66 to 99.88% and from 79.85 to 85.91%. In addition to nitrogen and phosphorus, the products also contain calcium in a plant-available form. In them, the sum of nutrient components (N + P_2O_5 + CaO) is 73.63-74.24%. The strength of their granules is 3.36-4.62 MPa. Such nitrogen-phosphorus fertilizers are highly concentrated and they are significantly superior to

amorphous in composition and properties. They can be applied during the feeding and sowing period.

Conclusion.

Thus, the principal possibility of obtaining concentrated unilateral phosphorus fertilizers for ploughing, where their efficiency will be the best, as well as concentrated NP fertilizers for application during the feeding and sowing period, is shown. This method allows the maximum use of raw materials in a single technological cycle with the simultaneous production of double, triple superphosphates and NP-fertilizers with high technical and economic indicators.

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