

**PHOSPHORUSSULFUR ACID TREATMENT OF HIGHCARBONATE
PHOSPHORITE FLOUR INTO ENRICHED SUPER PHOSPHATE**
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Abstract: the article presents the results of studying the process of obtaining enriched superphosphate by decomposition of carbonate phosphate flour mixtures of phosphoric acid by decomposition of carbonate phosphoric flour with mixtures of extraction phosphoric acid and sulfuric acid at ratios $SO_3: P_2O_5$ in them, equal to 1.2; 1.65; 2,6 and various ratios of mixture of acids: phosphoric flour. Under optimal conditions, the products obtained contain a relative content of a water-soluble form of P_2O_5 of at least 50%. And the strength of the granules fully meets the requirements of agriculture. The advantages of this process are shown in comparison with the production of ammonium sulfate phosphate.

Keywords: extraction phosphoric and sulfuric acids, phosphoric flour, decomposition, enriched superphosphate, composition.

**ФОСФОРНОСЕРНОКИСЛОТНАЯ ПЕРЕРАБОТКА
ВЫСОКОКАРБОНАТНОЙ ФОСФОРИТОВОЙ МУКИ В
ОБОГАЩЕННЫЙ СУПЕРФОСФАТ**

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Аннотация: в статье приведены результаты изучения процесса получения обогащенного суперфосфата путем разложения карбонатной фосфоритовой муки смесями экстракционной фосфорной и серной кислот при соотношениях $SO_3 : P_2O_5$ в них, равных 1,2; 1,65; 2,6 и различных соотношениях смеси кислот : фосфоритовая мука. При оптимальных условиях полученные продукты содержат относительно содержание водорастворимой формы P_2O_5 не менее 50%. А прочность гранул вполне отвечает требованиям сельского хозяйства. Показаны преимущества данного процесса по сравнению с получением аммоний сульфатфосфата

Ключевые слова: экстракционная фосфорная и серная кислоты, фосфоритовая мука, разложение, обогащенный суперфосфат, состав.

In 2016, the enterprises of the chemical industry of Uzbekistan produced 944.7 thousand tons of nitrogen, 143 thousand phosphate and 138 thousand tons of potash fertilizer calculated for 100% nutrients. As for phosphate fertilizers, they consist of ammophos (10% N; 46% P_2O_5), supraphos-NS (8-15% N; 20-24% P_2O_5), ammonium sulfate phosphate (15-19% N; 4-23% P_2O_5), feed ammonium phosphate (12% N; 53-55% P_2O_5), nitrocalcium phosphate (6% N; 16% P_2O_5), simple (1.5% N; 13.5% P_2O_5) and enriched (2.5% N; 18-26% P_2O_5) superphosphate. Of these, the last two types of product relate only to single phosphate fertilizers, and the rest to complex nitrogen-phosphate fertilizers. It should be noted that no complex fertilizer should be applied to the soil under autumn plowing. Since nitrogen is lost during the winter period with rain and melt waters. Therefore, it is necessary to increase the single phosphate fertilizers.

Simple superphosphate produces by sulfuric acid decomposition of natural phosphates, and enriched with a mixture of sulfuric and phosphoric acids. The difference between enriched superphosphate is that it is located between simple and double superphosphates in terms of P_2O_5 content. For its production, it is possible to use phosphate raw materials with a content of 20% P_2O_5 and more. Enriched superphosphate can be obtained on installations for the production of simple superphosphate with a slight change in mode of operation and the installation of additional devices.

When processing phosphate with phosphoric acid in the presence of increased norm of sulfuric acid complete decomposition of carbonate compounds occurs, opening the main mass of phosphate grains and a change in the crystalline structure of the undecomposed part of the phosphate, which in the presence of acid salts formed at the stage of ammonization of the pulp, and in the process of subsequent heat treatment at the stage of drying the product goes into a form accessible for assimilation by plants.

In Uzbekistan, Ammofos-Maxam has mastered on an industrial scale the production of nitrogen-phosphate fertilizer called Ammonium Sulfate Phosphate by ammonization mixtures of extraction phosphoric and sulfuric acids [1]. Depending on the consumer, there are three brands (A, B, C) of the product, each of two grades. Before that, under laboratory conditions, the properties of mixtures

of phosphoric and sulfuric acids were determined in a wide range of their ratios between themselves (SO_3 : P_2O_5 from 1.2 to 13.5) and the composition of the products their amonization [2, 3].

In the present work, to obtain an enriched superphosphate, it was decided to use three mixtures of extraction phosphoric and sulfuric acids with a ratio of SO_3 : $\text{P}_2\text{O}_5 = 1.2$; 1.65 and 2.6. The mixtures were prepared from extraction phosphoric acid with the composition (wt.%) 18.69 P_2O_5 ; 0.26 CaO; 0.64 MgO; 0.73 Al_2O_3 ; 0.46 Fe_2O_3 ; 2.72 SO_3 ; 1.02 F; 0.093 Cl and sulfuric acid with a concentration of 95%. Treatment with mixtures of acids was subjected to ordinary phosphoric flour of the composition (wt.%) 18.7 P_2O_5 ; 47.83 CaO; 15.3 CO_2 ; 1.24 Al_2O_3 ; 1.05 Fe_2O_3 ; 1.75 MgO; 2.00 F; 0.1 Cl.

The weight ratio of the mixture of acids: phosphoric flour ranged from 100: 30 to 100: 80, which corresponds to the norm of the mixture of acids with ratios $\text{SO}_3 / \text{P}_2\text{O}_5 = 1.2$ from 56 to 147%, $\text{SO}_3 / \text{P}_2\text{O}_5 = 1.65$ from 52 to 138% and $\text{SO}_3 / \text{P}_2\text{O}_5 = 2.6$ 40 to 105% with stoichiometry for the formation of $\text{Ca}(\text{H}_2\text{PO}_4)_2$. The duration of the interaction of the components was 15 min at 50°C. The resulting acidic phosphate pulp was ammoniated with ammonia gas to pH 3.8-4.0. Then they were dried first at 80°C and then at 105°C. Granulation of samples of wet phosphate masses was carried out in the process of drying by the method of rolling. Next, the dried samples were subjected to chemical analysis for the content of N and various forms of P_2O_5 according to known methods [4].

The results showed that an increase in the mass fraction of phosphoric flour relative to the mixture of acids, on the one hand, increases the content of the total form of phosphorus, on the other hand, significantly reduces the nitrogen content and the relative forms of assimilable and water-soluble phosphorus. An increase in the proportion of sulfuric acid in a mixture with phosphoric acid to the ratio SO_3 : $\text{P}_2\text{O}_5 = 1.65$ and 2.6 with an increase in the proportion of processed phosphoric flour from 10 to 80 leads to an even greater decrease in the above indicators. In any case, with the studied ratios of SO_3 : P_2O_5 and the mixture of acids: phosphoric flour, samples of enriched superphosphate with a minimum nitrogen content (from 1.14 to 5.41% N) are obtained and quite suitable as a one-sided phosphate fertilizer for making under the ploughland.

Agrochemists value phosphorus-containing fertilizers, the relative content of a water-soluble form of P_2O_5 is at least 50%. Fertilizer with this indicator is obtained when the ratio of the mixture of acids: phosphoric flour = 100: 60. In this case, at a ratio SO_3 : $\text{P}_2\text{O}_5 = 1.2$, the composition of the enriched superphosphate looks as follows (wt.%): P_2O_5 total - 25.30%, P_2O_5 ass. : P_2O_5 total = 86.0%, P_2O_5 wat. : P_2O_5 total = 56.4%, N - 2.65%, and for SO_3 : $\text{P}_2\text{O}_5 = 1.65$ - P_2O_5 total - 23.25%, P_2O_5 ass. : P_2O_5 total = 80.39%, P_2O_5 wat. : P_2O_5 total = 51.4%, N - 2.21%. When using a mixture of acids with the ratio SO_3 : $\text{P}_2\text{O}_5 = 2.6$, only when the mass ratio of the mixture of acids: phosphoric flour is 100: 50, in the product P_2O_5 wat. reaches 50%. In this case, the product contains P_2O_5 total - 19.83%, P_2O_5 ass. : P_2O_5 total = 79.27%, P_2O_5 wat. : P_2O_5 total = 46.29%, N - 2.73%. At the same time, the granules of these products have a granule strength of at least 3 MPa and fully meets the requirements of agriculture.

We calculated material balances for obtaining 100 kg of P₂O₅ in the form of three grades of ammonium sulfate phosphate and three grades of new phosphate-containing fertilizers, obtained by decomposition of phosphoric flour mixtures of phosphoric and sulfuric acids with a mass ratio of the mixture of acids: phosphoric flour, equal to 100: 50. Their comparison indicates the significant advantages of the second method of producing fertilizers. Compared with the production of ammonium sulfate phosphate, the decomposition of phosphoric flour with mixtures of sulfuric and phosphoric acids can significantly reduce the consumption of such expensive starting components as extraction phosphoric acid, sulfuric acid and ammonia.

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