Enriched Superphosphate and Ammophosphate Fertilizer Based on Washed Dried Phosphorite Concentrate

A. A. Rasulov and B. E. Sultonov

Namangan State University, Republic of Uzbekistan, Uzbekistan.

Keywords: Sulfuric and phosphoric acid; washed dried concentrate; decomposition; ammonization; separation; enriched superphosphate and ammophosphate; chemical and salt compositions and material balance.

ABSTRACT

Development of a technology for obtaining enriched superphosphate and ammophosphate by processing washed and dried phosphorite concentrate (WDPC) in a single cycle. The optimal ratio $\text{P}_2\text{O}_5_{\text{WPPA}}:\text{H}_2\text{SO}_4_{\text{meh}} : \text{P}_2\text{O}_5_{\text{WDPC}} = 1:0.28:0.08$ was found, at which the composition and properties of ammophosphate fertilizer are maximally improved and a single phosphorus fertilizer is additionally obtained. It has been established that on the basis of the solid part of the ammophosphate pulp, samples of enriched superphosphate are obtained with the following indicators (wt., %): $\text{P}_2\text{O}_5_{\text{t.}} = 30.16-32.01; \text{P}_2\text{O}_5_{\text{as. c. a.}} : \text{P}_2\text{O}_5_{\text{t.}} = 98.54-100; \text{P}_2\text{O}_5_{\text{water solubility (w.s.)}} : \text{P}_2\text{O}_5_{\text{t.}} = 54.3-55.5; \text{N} = 5.45-6.04$. A sample of ammophosphate contains (wt., %): $\text{P}_2\text{O}_5_{\text{t.}} = 52.43-53.31; \text{P}_2\text{O}_5_{\text{water solubility (w.s.)}} : \text{P}_2\text{O}_5_{\text{t.}} = 87.41-88.36; \text{CaO} = 3.04-4.26; \text{N} = 13.65-14.03$ and $\text{SO}_3_{\text{t.}} = 4.37-10.74$. Ammophosphate consists of mono- and diammonium phosphate, ammonium sulfate and dicalcium phosphate. Superphosphate also contains activated phosphorite, complex salts and gypsum. The material balance of the process of their production in a single technological cycle has been calculated.
1. INTRODUCTION

The consumption of phosphoric acid for the production of ammonium phosphates, in particular ammophos, can be reduced if a certain amount of natural phosphate (apatite or phosphorite) is dissolved in the acid supplied for ammonization. The work [1] shows the conditions for obtaining ammophos with a reduced consumption of H₃PO₄ and studied the effect of natural phosphate from the Mazydag deposit (Turkey), containing, %: P₂O₅ – 28.2; CaO – 40.7; MgO – 0.59; Fe₂O₃ – 6.40; Al₂O₃ – 3.0; others - 15.5 for the composition and properties of the finished product.

It has been revealed that partial replacement of phosphoric acid P₂O₅ with natural phosphate P₂O₅ makes it possible to reduce H₃PO₄ consumption by 4-5% in the production ammophos of grade 1 and accordingly reduce the cost of the product, as well as slightly improve its physical and mechanical properties.

This approach makes it possible to use secondary phosphate raw materials in the production of ammophos.

In the 80-90s of the last century, in order to reduce the consumption rates of the acid reagent for the production of 1 ton of P₂O₅ in ammophos and expand the range of concentrated fertilizers, Russia’s specialists developed the technology of a new nitrogen-phosphorus fertilizer - ammophosphate, which contains 43% of nutrients [2,3]. Ammophosphate belongs to the class of partially decomposed phosphates. The process of its production is based on decomposition of natural phosphates by a high rate of H₃PO₄ (150-200% of stoichiometry), followed by neutralization of acidity with ammonia, granulation and drying of the product [2]. The phosphate component of ammophosphate is monoammonium phosphate, and as impurities, dicalcium phosphate and basic calcium phosphates such as hydroxyfluorapatite and unreacted phosphorites, as well as complex salts that fall into the solid phase when ammonizing excess wet process phosphoric acid (WPPC).

In this case, a list of chemical compounds can be provided, the formation of which is possible during ammonia neutralization of extraction phosphoric acids with different composition and content of impurities [3-6]. Thus, in the range pH = 2.5-5.5, the following compounds are formed:

\[ \text{NH}_4\text{H}_2\text{PO}_4; \quad (\text{NH}_4)_2\text{SO}_4; \quad \text{MgHPO}_4; \quad \text{MgNH}_4\text{PO}_4; \quad \text{H}_2\text{O}; \quad \text{Mg(Fe,Al)(NH}_3)_2(\text{HPO}_4)_2\text{F}_3; \quad \text{Mg}_2(\text{NH}_3)_2(\text{HPO}_4)_4; \quad 8\text{H}_2\text{O}; \quad \text{MgNH}_4\text{HFPO}_4; \quad (\text{Fe,Al})\text{NH}_4(\text{HPO}_4)_2; \quad 0.5\text{H}_2\text{O}; \quad (\text{Fe,Al})\text{NH}_4\text{HPO}_4\text{F}_2; \quad \text{SiO}_2; \quad \text{CaHPO}_4; \quad \text{Ca}_5(\text{PO}_4)_3\text{OH}. \]

All phosphates are citrate soluble except hydroxylapatite.

Neutralization of WPPC in the presence of ammonium fluoride or silicofluoride can lead to the formation of a number of fluorides Fe, A1, Ca, Mg. In the absence of ammonium fluorides and silicofluorides, hydroxides are formed. They are significantly degrade the quality of the finished product.

In order for improve the quality of ammophosphate, that is, to increase the content of total (t.) and water soluble(w.s.) phosphorus in it, it is necessary to clean the pulp from solid suspensions, magnesium compounds and one and a half oxides (Fe₂O₃, Al₂O₃ and others).

This can be accomplished by separating the ammophosphate pulp into solid and liquid phases. The solid phase is nothing more than concentrated enriched superphosphate, and the liquid phase after preammonization, granulation and drying is high-quality ammophosphate.

The essence of this process is the decomposition of phosphate raw materials with phosphoric acid; separation of acid phosphate pulp into liquid and solid phases; granulation and drying of the solid phase by pelleting to obtain a single phosphorus fertilizer such as enriched superphosphate; ammonization of the liquid phase with ammonia to pH = 4.0-4.5 followed by granulation and drying of the product on cylinder granulator drier (CGD) with obtaining a nitrogen fertilizer such as ammophosphate.

This approach is made in [7], where two different types of product are obtained in one cycle. This work uses mineralized mass (MM - 14.33% P₂O₅) and WPPC with a content of 14.32% in the range of weight ratios P₂O₅ : P₂O₅ to MM from 1: 0.38 to 1: 0.165. It is shown that after separation of phosphate acid-phosphate pulp and drying its solid part, enriched superphosphate of the composition (wt., %) was obtained: 30.57-32.53 P₂O₅; 26.78-31.02 CaO; P₂O₅ : P₂O₅ : P₂O₅ = 59.42-65.14; P₂O₅ to MM = 13.54-36.30 and CaO to MM : CaO = 41.38-47.45% and on the basis of the liquid part of the pulp after its ammonization to 4.5 and drying, an ammophosphate was obtained, containing (wt., %): N from 6.54 to 9.12%; P₂O₅ from 47.62 to 56.
In this work, X-ray analysis was performed on a XRD-6100 diffractometer (Shimadzu, Japan) to determine the salt composition of both products. CuKα emission (β filter, Ni, tube current and voltage mode 30 mA, 30 kV) and constant detector rotation speed 4 deg/min were used, and the scanning angle varied from 4 to 80°. The interpretation and identification of mineral phases was carried out using catalogs [15, 16].

3. RESULTS AND DISCUSSION

The results of chemical analysis established that the optimal ratio of P₂O₅/WPPA: H₂SO₄/WH₁: P₂O₅/WDCP 1: 0.28: 0.08 can be considered and the pulp pH is 2.5-3. At the same time, samples of enriched superphosphate are obtained on the basis of the following parameters (wt., %): P₂O₅ - 30.16-32.01; CaO - 11.43-12.01; MgO - 0.25-0.84; Al₂O₃ - 1.82-2.51; Fe₂O₃ - 0.46-1.13; SiO₂ - 5.45-9.45; SO₃ - 51.74-95.74.

The addition of WDPC to WPPA is explained by the fact that pure phosphoric acid decomposition does not provide the maximum development of the phosphate mineral. Decomposition of WDPC was performed at mass ratio of P₂O₅/WPPA: H₂SO₄/WH₁: P₂O₅/WDCP from 1: 0.11: 0.12 to 1: 0.28: 0.12 at 70°C for 60 minutes.

Before filtration, phosphoric acid gypsum slurries (PAGS) were ammonized to pH = 1.6; 2.0; 2.5 and 3.0. Then they were separated into liquid and solid phases by vacuum filtration. The residue remaining on the filter was dried. The filtrate, i.e. the liquid phase, was further ammonized to pH = 5 and dried. Granulation of products, obtained from the solid phase and the liquid phase was carried out during the drying process by method of pelleting.

The products were subjected to conventional procedures [13]. Form of N total (t) was determined by method Kjeldahl's nitrogen [14]. The acceptable forms of P₂O₅ and CaO were determined by citric acid, the pH of the pulp was measured by laboratory ion meter I-130M.

In this work, the composition of P₂O₅, CaO, MgO, Al₂O₃, Fe₂O₃, SiO₂, SO₃, and the ratio of P₂O₅/WPPA: H₂SO₄/WH₁: P₂O₅/WDCP were determined. The composition of products P₂O₅/WPPA: H₂SO₄/WH₁: P₂O₅/WDCP 1: 0.28: 0.08 can be considered and the pulp pH is 2.5-3. At the same time, samples of enriched superphosphate are obtained on the basis of the following parameters (wt., %): P₂O₅ - 30.16-32.01; CaO - 11.43-12.01; MgO - 0.25-0.84; Al₂O₃ - 1.82-2.51; Fe₂O₃ - 0.46-1.13; SiO₂ - 5.45-9.45; SO₃ - 51.74-95.74.

The purpose of this research work is to obtain high-quality ammonophosphate and enriched superphosphate from low grade phosphate raw materials.

2. METHODS AND MATERIALS

In our works [10-12], we studied the process of producing enriched superphosphate and ammonophosphate using the example of washed dried phosphorite concentrate (WDPC) - phosphorite products used to obtain washed and burned concentrate. It contains (wt., %): 26.08 P₂O₅; P₂O₅/WPPA: P₂O₅/WDCP = 13.11; 51.74 CaO; 0.89 MgO; 0.31 Fe₂O₃; 1.02 Al₂O₃; 1.59 SO₃; 9.95 CO₂; 3.41 F; 2.51 insoluble reduce (i.r.). For its decomposition was used WPPA contained (wt., %): 7.92 P₂O₅; 0.21 CaO; 0.30 MgO; 0.56 Al₂O₃; 0.45 Fe₂O₃; 1.83 SO₃; 1.53 SO₃free and 93.5% sulfuric acid.

The purpose of this research work is to obtain high-quality ammonophosphate and enriched superphosphate from low grade phosphate raw materials.
Расулов и Султонов

CSIJ, 31(3): 55-61, 2022; Article no. CSIJ.92538

Р2О5а.c.a: Р2О5tl. = 98.54-100; Р2О5w.s.: Р2О5tl. = 54.3-55.5; N - 5.45-6.04 and quite suitable as an effective phosphorus fertilizer for a ploughed land.

Under the conditions found from the liquid part after its extra ammonization (pH = 5), the obtained ammophosphate fertilizers have (wt., %): Р2О5tl. - 52.43-53.31; Р2О5а.c.a.: Р2О5tl. = 94.81-96.27; Р2О5w.s.: Р2О5tl. = 87.41-88.36; СаОtl. - 4.01-4.26; СаО а.c.c.a. - 3.74-3.87; N - 13.65-14.03 and SO3tl. - 4.37-10.74. The latter component represents a water soluble (NH4)2SO4 and calcium represents a citrate-soluble CaHPO4.

Balakhovo production association (PA) "Minudobreniya" in Russia produces ammonium phosphate of the highest brand A. Its composition (mass., %): N 9.78; Р2О5tl. 50.25; Р2О5а.c.a. 47.60; Р2О5w.s. 40.0. The quality of the ammophosphate fertilizers we obtain is not inferior to it, and in some parameters they are even superior.

Fig. 1 shows an X-ray pattern of enriched superphosphate obtained at the ratio P2O5WPPA : H2SO4аmн.: P2O5WDPС = 1 : 0.28 : 0.08. Analyzing the roentgenograms, it can be concluded that the dried solid phase consists of monoammonium phosphate (5.29; 3.73; 3.06; 2.64; 2.00 Å), monocalcium phosphate (4.92; 2.85 Å), dicalcium phosphate (3.38 Å), activated fluoroapatite (3.48; 3.17; 2.76; 2.71; 1.84 Å) and gypsum of different forms (6.29; 6.00; 3.01; 2.80 Å).

The phase composition of the ammonium phosphate fertilizer (Fig. 2) is represented by monoammonium phosphate (5.30; 3.74; 3.06; 2.65; 2.00 Å), diammonium phosphate (5.20 Å), dicalcium phosphate (4.32 Å), ammonium sulfate (5.38; 4.32-4.38; 2.36 Å). At the same time, lanes 5.30; 3.06; 2.65 Å refers to both sulfate and ammonium phosphate.

Based on laboratory experiments, the material balance of enriched superphosphate and concentrated ammophosphate in a single technological cycle is calculated (Fig. 3).

![Fig. 1. Radiograph of enriched superphosphate on base solid part of ammophosphate pulp](image-url)
Fig. 2. Radiograph of concentrated ammophosphate fertilizer based on liquid part of ammophosphate pulp

Fig. 3. The material balance of enriched superphosphate and concentrated ammophosphate in a single technological cycle
4. CONCLUSION
The process of obtaining concentrated grades of enriched superphosphate and ammonophosphate by separating phosphorus-sulfur acid decomposition products of washed dried concentrate into solid and liquid phases has been studied. The optimal ratio of P₂O₅_{SWPPA}: H₂SO₄_{amb.:} P₂O₅_{SWDPC} is 1: 0.28: 0.08 and the pulp pH is 2.5-3. X-ray research of both dried phases was performed. The solid phase is represented by mono- and diammonium phosphates, mono- and dicalcium phosphates, activated phosphorite and gypsum. The dried ammonophosphate mainly contains mono- and diammonium phosphates, ammonium sulfate and dicalcium phosphate. The latter component is exclusively in a citrate-soluble form. A process flow diagram was developed and the material balance of enriched superphosphate and ammonophosphate in a single process cycle was calculated. The some superior parameters of ammonophosphate are: good commodity properties (granularity, granule hardness), good water solubility and content other nutrient components (sulfur and calcium).

COMPETING INTERESTS
Authors have declared that no competing interests exist.

REFERENCES
12. Rasulov AA, Kholmurudov JE, Seytnazarov AR, Beglov BM, Namazov ShS. Enriched superphosphate based on phosphoric acid gypsum pulp and carbonate phosphorite flour. LI International Correspondence Scientific and Practical Conference. European research: Innovation in Science,


