



Development of The Technology for Obtaining Magnesium-Modified Phosphorus Fertilizer

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ABSTRACT

Characteristic properties of crystalline structure of magnesium-modified phosphorus fertilizers have been investigated, the possibility of the change in the salt content of the solid phase in the decomposition process and magnesium superphosphate consisting of mono-calcium phosphate along with mono-magnesium phosphate have been determined. A new efficient technology is proposed for obtaining magnesium-modified phosphorus fertilizers on the basis of classic superphosphate technology by partly replacing the phosphate raw material with the magnesium carbonate raw material, dolomite.

Keywords: *phosphorus fertilizer, technology, magnesium modification*

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INTRODUCTION

The following problems have been considered to be solved in connection with carrying out the intended research work:

- studying physics-chemical properties of technological phases of decomposition of phosphate raw material in sulfuric acid with the participation of dolomite; studying the process of obtaining magnesium superphosphate according to the results of physics-chemical and technological research of phosphate raw material decomposition in pure sulfuric acid separately by partly replacing them with dolomite; investigating the mechanism of the process of obtaining magnesium-modified phosphorus fertilizer by separately processing waste dolomite with sulfuric acid in order to improve physical properties of the fertilizer, maximum replacement of phosphate raw material with magnesium carbonate raw material; development of efficient technologies for obtaining magnesium-modified phosphorus fertilizers according to technical indicators; controlling the developed technologies for obtaining magnesium-modified phosphorus fertilizers in industrial testing facility; studying agrochemical efficiency of magnesium-modified phosphorus fertilizers obtained on the base of the proposed technologies [1-2].

As it is known, being a complicated process, obtaining superphosphate on the basis of phosphate raw materials (apatite and phosphorites) contains the interaction of initial raw material first with sulphate and then formed sulfuric acid. Decomposition rate of phosphate raw material with sulfuric acid is determined by the initial rate of the raw material decomposition depending on two main factors – acid activity and density of free hydrogen ions in phosphorus fertilizers production [3-5].

Using fine grained phosphorite makes it possible to increase its decomposition rate and obtaining ratio of superphosphate regardless of MgO:P₂O₅ ratio in initial phosphorite. And it shows that, the rate of decomposition process of phosphorite with sulfuric acid is determined by diffusion of acid to the surface of phosphorite along with the density of H⁺ ions in high value of MgO:P₂O₅ ratio. However, diffusion process is determined by a solid phase decomposed on the surface of phosphorite in the form of layers, i.e. micro-crystalline structure of calcium sulfate, and depends on its dispersion and crystallization condition. However, crystallization condition is characterized by the saturation rate of the system with CaSO₄ in various values of acid density, rate, temperature [6-7].

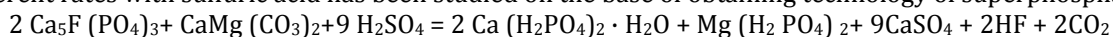
MATERIALS AND METHODS

Chemical processing of both apatite and phosphorite ores by phosphorus-containing products have specific properties depending on their structures and mineralogical compositions. Thus, phosphorite ores differ from apatite ones by high dispersion of phosphate mineral contained by them and the amount of mixtures. Namely, due to high dispersion, special surface of phosphorite is great relative to apatite and during the interaction with acids they decompose relatively quick to apatite ones. However, during decomposition of phosphorites with acids, most of the mixtures (Fe_2O_3 , Al_2O_3 ; MgO and etc) contained by them transform into liquid phase so that, it decreases the quality of the fertilizer and increases the loss of phosphate anhydride. Ferrous phosphates transformed into liquid phase form saturated solutions being stable for a long time. Therefore, while being obtained on the base of apatite, decomposition rate of superphosphate is 94% after 21 days and 90% in phosphorite. Apatite has been used as a phosphate raw material in our research.

RESULTS AND DISCUSSION

The impact of apatite and dolomite ratios as the technological parameters, the sequence of the process, mixing time of the reagents, rate, density and temperature of the sulfuric acid on the decomposition process has been studied in order to solve the intended problem.

For this purpose, decomposition process of the dolomite mixture and the apatite concentrate taken at different rates with sulfuric acid has been studied on the base of obtaining technology of superphosphate.



As decomposition properties of apatite and dolomite with sulfuric acid are varied, the research works have been carried out in 3 variants - with the addition of a mixture of apatite and dolomite to the decomposition process in turns, as well as separately.

Decomposition process has been carried out in different mass ratios of apatite and dolomite, stoichiometric rate and densities (30-66%) of H_2SO_4 .

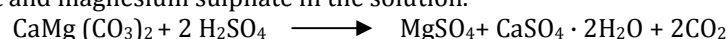
The comparison of the impact of addition sequence of apatite and dolomite to the decomposition on the process shows that during the decomposition of raw materials with sulfuric acid by being mixed, decomposition rate of the initial process has low value and regardless of continuous mixture, almost no increase is observed in its value. The addition of the dolomite with a phosphate raw material to the decomposition process with acid has negative impact on both the amount of formal P_2O_5 and total decomposition rate of a phosphate raw material so that, it is related to the participation of magnesium in the dolomite.

Being solved in phosphate, MgSO_4 generated in such a system decreases its reaction capacity, i.e. the activity of H^+ ions and apatite decomposition doesn't go till the end. Thus, the increase of decomposition rate value becomes weak at the next stages. Despite the fact that CaSO_4 crystals are obtained in a large disperse form compared to the previous ones, such cases are more prominent in systems dominated by the solid phase.

In the second option of the processing of raw materials, i.e. addition of first apatite, then dolomite with sulfuric acid to the decomposition, as well as, at the same condition the value of decomposition rate of phosphate raw material is observed to be high relative to previous version. This is due to the fact that, at the first moment of the decomposition apatite concentrate reacts with residual amount of sulfuric acid. At this time, favorable conditions are possible for obtaining phosphate acid.

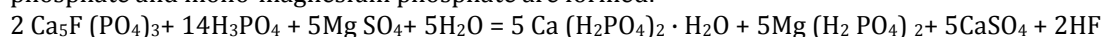
The analysis of the results obtained from the two proposed options allows to conclude that, dolomite is more likely to be added to the resulting suspension after the decomposition of the major part of the apatite.

The third option for the processing of raw materials is based on the separate decomposition of both apatite and dolomite with sulfuric acid and the combined processing of the obtained solid solutions. However, at this time it is possible to decrease the amount of CaSO_4 ballasting in the fertilizer by separating CaSO_4 , obtained during the decomposition of the dolomite with sulfuric acid, from the solution. Thus, unlike apatite, decomposition of the dolomite with sulfuric acid results in the formation of calcium sulphate in sediment and magnesium sulphate in the solution.



In this case, the decomposition of dolomite in the system occurs with the presence of MgSO_4 , which is capable of precipitating them, in the formation of large dispersed CaSO_4 crystals on existing crystal centers. Therefore, depending on the time, the change in the value of decomposition rate at low ratio of the dolomite in raw material mixture is compatible with obtaining condition of superphosphate on the base of the only apatite.

After mixing the solid solutions obtained from the decomposition of apatite and dolomite with sulfuric acid, the second stage of the process starts, that is, the non-decomposable portion of the apatite and dolomite is going to be dissolved in the presence of $MgSO_4$ by phosphate acid until mono-calcium phosphate and mono-magnesium phosphate are formed:



The formed mono-calcium and mono-magnesium phosphates are observed in the solution and they are crystallized by its saturation.

New technological scheme for obtaining magnesium-modified phosphorus fertilizers by replacing apatite concentrate with partial dolomite on the basis of the proposed methods is given in Figure 1.

75% sulfuric acid passes through the flow meter 7 to the diluting tank 13 of sulfuric acid. Water flows here through the water tank 6 via the flow meter 8. Diluted sulfuric acid is transmitted to the stirring rod 4. The apatite passes through the bunker 1 and doser 2 and enters here via the transporter 3. Some acid is transmitted to the other stirring rod 12 via the diluted sulfuric acid tank 13. The dolomite enters there by means of the transporter 11 passing through the bunker 9 to the dozer 10. $MgSO_4$ solution main filtrate capacity 18 separated by notch filter 17 from the decomposition of solid solution and decomposition of the dolomite and apatite with sulfuric acid, is transmitted to the stirring rod 14, the mixture obtained from the mixing of both solid solutions enters the superphosphate chamber 15 working without any interruption. The fertilization process in the superphosphate chamber is maintained within 1.5 hours at 105-110^o C. The chamber superphosphate is transmitted to the scatter 19 through the ribbon transporter 16, and then to the warehouse 20. Within 7 days of the storage, being neutralized the powdered product is transmitted for being granulated. The granulation process was carried out in accordance with the common mode of granular superphosphate production. This process consists of several stages: neutralization of free phosphate acid with limestone, hydration and granulation of neutralized fertilizer, drying of fractions, grinding of large fractions and returning to the process. The amount of the fraction is about 20-30%.

The powdered fertilizer 20 is transmitted to the bunker 22 by means of a bucket crane 21, and from there via ribbon dozer 23 it is transmitted to the sieve working with vibration principle. At the same time, here the limestone (2-4% of total fertilizer) is continuously transmitted from the other bunker 25 and the neutralization process begins. The amount of limestone is regulated by the dozer 26. By means of vibration sieve, large particles of greater than 5 mm are separated and grained in the granulator 24 and stored in a neutralized fertilizer bunker 28 via the transporter 27. Magnesium superphosphate, passed through the neutralization process, is transmitted to a granular drum 30 by means of the transporter 29.

Grinding of the neutralized product is carried out in horizontal rotating granular drum. Fertilizers are hydrated up to 16-18% by the water given from a special sprayer installed inside the drum and the fertilizer particles hydrated as a result of drum rotation are granulated. The duration of the fertilizer in the granular drum is about 8-12 minutes. Then, the wet grains are dried in the drying drum 31 at the expense of the heat of the stoves up to 3-5% moisture. The dried product is transmitted to the sieve 33 by means of the elevator 32, standard grains with 2-4 mm are supplied as ready made products, large-sized fractions are grinded up in the granulator 34 and re-processed in small dimensions. The ratio of apatite concentrate and dolomite, the rate, density and amount of sulfuric acid used for the decomposition of both apatite and dolomite were taken in accordance with optimal quantities determined during laboratory experiments. The obtained granular superphosphate was analyzed by standard methods according to their main components. The test conditions are given in Table 1. The industrial trial results of the process for obtaining magnesium superphosphate on the basis of apatite concentrate and dolomite have confirmed the results of the laboratory researches.

Table 1: The condition for carrying out the process

Raw material		Consumption rate (1 t superphosphate), ton				The temperature of sulfuric acid, °C	
Apatite	Dolomite	Apatite	Dolomite	Sulfuric acid supplied for apatite decomposition	Sulfuric acid supplied for dolomite decomposition	In the entry of apatite mixer	In the entry of dolomite mixer
85	15	0.410	0.070	0.271	0.076	60	62
80	20	0.380	0.095	0.252	0.101	62	62
75	25	0.350	0.117	0.233	0.124	62	62
70	30	0.320	0.139	0.214	0.146	60	60

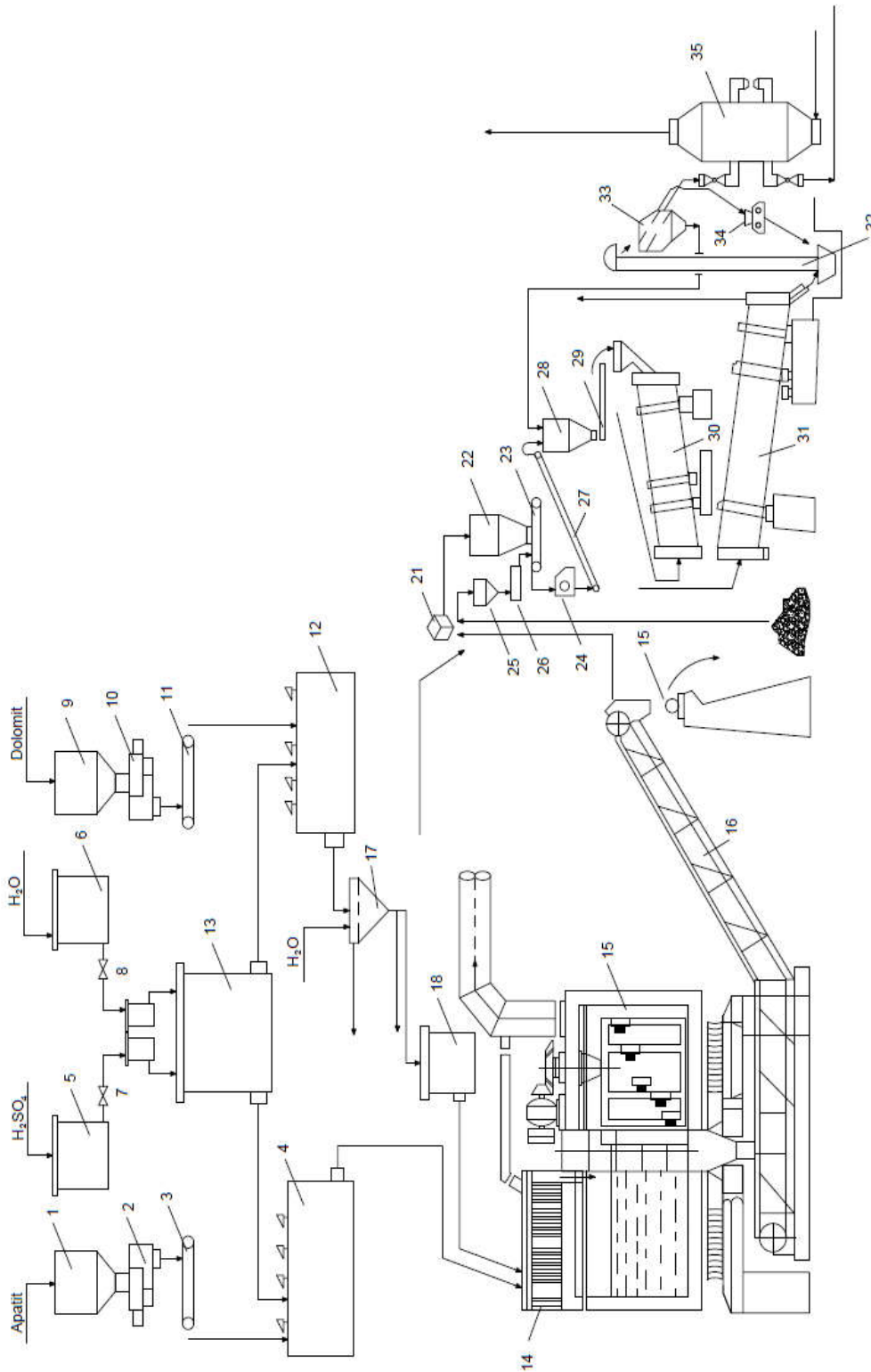


Figure 1. Technological scheme of magnesium-modified phosphorus fertilizers production: 1. Apatite bunker; 2, 10- dozers; 3, 11, 23, 27, 29 –transporters; 4- a stirring rod for apatite decomposition; 5- a tank for H₂SO₄; 6 – a tank for H₂O; 7,8 –flowmeter; 9- a bunker for the dolomite;12- a stirring rod for dolomite decomposition; 13- a tank for diluting phosphate acid; 14- a stirring rod for solid solutions; 15- superphosphate chamber; 16 - ribbon transporter; 17- a notch filter; 18- main filtrate capacity; 19- scatter; 20- storehouse; 21 - bucket crane; 22 –a bunker for superphosphate; 25 –a bunker for neutralizing additives; 24, 34 – grainers; 28 – a bunker for neutralized superphosphate; 30 – granulator; 31 – a drier drum; 32- elevator; 33 – sieve; 35 – boiler

Table 2 shows the indicators of the chamber product and ripe magnesium superphosphate obtained on the base of apatite concentrate and dolomite.

Table 2: The indicators of the magnesium superphosphate obtained on the base of apatite concentrate and dolomite

The amount of the raw material (total amount k.h.)		Indicators						
Apatite	Dolomite	P ₂ O ₅			H ₂ O	MgO	Total amount of nutritional elements	Decomposition rate of phosphate raw material
		Total	Assimilated	Consumed				
Chamber product								
85	15	16.53	15.28	8.01	12.01	1.45	16.73	92.40
80	20	16.35	15.01	8.72	12.57	1.93	16.94	91.82
75	25	16.25	14.74	9.40	13.61	2.17	16.91	90.70
70	30	16.06	14.31	10.32	14.51	2.83	16.14	89.20
Ripe product*								
85	15	17.79	17.02	4.12	8.91	1.95	18.97	95.68
80	20	17.74	16.90	4.95	9.14	2.35	19.15	95.36
75	25	17.24	16.35	5.23	9.78	2.99	19.34	94.82
70	30	17.13	16.14	5.90	10.50	3.13	19.27	94.24

*ripening period 7 days

Separate decomposition of the apatite and dolomite with sulfuric acid and the combined processing of the obtained solid solutions makes it possible to replace the 20-30% of apatite with local magnesium raw material - dolomite, reduce the storage period of the product from 24 days to 7 days by achieving high decomposition rate of the raw material, achieve the superphosphate enrichment with added nutritional magnesium, and obtain economic-ecological benefits.

A new efficient technology is proposed for obtaining magnesium-modified phosphorus fertilizers on the basis of classic superphosphate technology by partly replacing the phosphate raw material with the magnesium carbonate raw material, dolomite.

Research has been discussed at the Department of Oil and Gas Equipment and it is recommended to print on the basis of copyright. The issue is new and new effective technology is available to obtain magnesium-modified phosphorus fertilizers for use in modern technologies.

CONCLUSION

The objective laws of decomposition process of the apatite in sulfuric acid with the presence of dolomite have been studied. It has been determined that based on existing superphosphate technology, the decomposition process is suitable for obtaining a common superphosphate during dolomite replacement with a maximum of 15% of the phosphate raw material. It has been shown that due to the increase in the amount of dolomite in the composition of the raw material, the reason for decreasing the decomposition process is that dolomite decomposition is quick relative to apatite thanks to their crystalline structure properties, diffusion of the acid to dolomite is law relative to apatite and the negative effect of magnesium compounds on the diffusion processes in the system.

Acceleration of the diffusion process during the separate decomposition of apatite and dolomite in sulfuric acid, transformation of Mg salts and P₂O₂ into soluble form and the increase in decomposition rate have been determined.

Due to the formation of soluble forms of Ca and Mg salts in the decomposition process of apatite and dolomite minerals separately with sulfuric acid, the decrease in the amount of CaSO₄ ballasting in the fertilizer has been determined.

Characteristic properties of crystalline structure of magnesium-modified phosphorus fertilizers have been investigated, the possibility of the change in the salt content of the solid phase in the decomposition process and magnesium superphosphate consisting of mono-calcium phosphate along with mono-magnesium phosphate have been determined.

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