Phosphoric Acid Decomposition of Phosphorite with Partial Replacement of Its Sulfuric Acid

Arislanov Akmalzhon Sayibbaevich, Shamshidinov Israiljon Turgunovich, Ergashev Oybek Karimovich

Senior lecturer at Namangan Institute of Engineering and Technology;

Doctor of technical sciences, Professor, Namangan Institute of Civil Engineering;

Doctor of chemical sciences, Namangan Institute of Engineering and Technology.

ABSTRACT: This article initiate that in the phosphoric-sulfuric acid decomposition of secondary phosphate (used by EPC concentration 21% P_2O_5 and 30-35% P_2O_5) optimal are the weight ratio of EPA (100% P_2O_5): H_2SO_4 : phosphorite = 1,3:0,2:1,0, temperature 60^oC, decomposition time 2 hours, ammonization at 80^oC to pH about 2, drying at 105^oC. Get NPS fertilizer containing P_2O_{5tot}=44-45%, P_2O_{5int}=4,00-44,2%, $P_2O_{5time.}$=37,0-37,5%, N=2,5-3,0%, SO_{3tot}=9,0-9,3%, $SO_{3time.}$=6,3-6,7% and others. K_p=88-90%, a K_{SO3} = 68-72%. At the same time, the consumption per unit of output is reduced by sulfuric acid by 15-25% for ammonia by 60-70%, the cost is reduced by 20-25%.

KEYWORDS: phosphoric-sulfuric acid decomposition, phosphorite, sulfuric acid, phosphoric acid, NPS fertilizer, sulfosuperammophos, retrograde.

I. INTRODUCTION

During phosphorus-sulfuric acid decomposition, neutralization of the acid product with gaseous ammonia to a pH of 3.5-4.5 does not take into account the retrograde of assimilable phosphorus and the conversion of water-insoluble calcium sulfate to water-soluble ammonium sulfate. Therefore, we set the task of studying the optimal amount of sulfuric acid introduced into the EPA, the pH of the solution, and the degree of conversion in the process of ammonization of acidic pulp. And in our experiments, we used activated EPA with ammonium nitrate and a mixture with sulfuric acid.

For the experiments used phosphorites of Karatau, composition, in mass %:

P_2O_5=25,3; CaO=40,4; MgO=2,6; Fe_2O_3=1,24 Al_2O_3=1,04; F=2,0; CO_2=6,9.

In addition, unpaired was used to decompose phosphorite (21,5% P_2O_5) and evaporated to 24.9-34.66% with the introduction of ammonium nitrate EPA with a partial replacement of EPA (calculated on P_2O_5) sulfuric acid in an amount 10-25%.
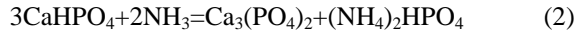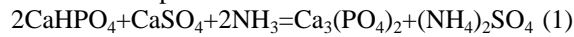
II. METHODS OF RESEARCH

The decomposition process was carried out in a thermostated three-necked flask with a water lock at a temperature of 60 ° C for hours. Then, the acidity of the pulp was neutralized with gaseous ammonia in the range of pH = 1.7-3.4. The pulp was listened at a temperature of 105 ° C. Depending on the concentration of acid used and acidity, the moisture content in the product ranged from 0.16 to 7.2% i.e. drying processes occurred at different speeds. During the experiment, we identified three forms P_2O_5 by weight analysis method, SO_3 precipitation method, pH on a pH meter.
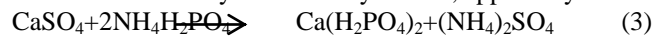
Phosphorite decomposition factors determined (K_p) acid and ammoniated pulp and solid product, the conversion of the resulting calcium sulfate during the decomposition of phosphorite into ammonium sulfate (for example, a water-soluble form SO_3– indicated by K_{SO3}) when neutralizing the pulp with ammonia. The initial parameters were taken in this way: the weight ratio of EPA (100% P_2O_5) to phosphorite 1.5: 1 and 10-25% it was replaced by sulfuric acid and others EPA (100% P_2O_5): H_2SO_4=1,4:0,1/1,25:0,25 the concentration of the original EPA was taken from 20 to 35% P_2O_5

The results show that the process of decomposition of phosphorite decomposition coefficient (K_p) in weak (21,5% P_2O_5) EPA is 49.33% (without activation with ammonium nitrate), water-soluble sulfates account for 60.5%.

After drying the pulp K_p increases to 62.34% due to the additional decomposition of phosphorite. As the pulp is neutralized with ammonia K_p falls due to reversible processes:

$$2CaHPO_4+CaSO_4+2NH_3=Ca_3(PO_4)_2+(NH_4)_2SO_4 \quad (1)$$
$$3CaHPO_4+2NH_3=Ca_3(PO_4)_2+(NH_4)_2HPO_4 \quad (2)$$

And the degree of conversion of sulfates increases. When administered with weak (21,5% P_2O_5) EPC ammonium nitrate, K_p in acidic pulp increases by 30% (K_p in acidic pulp 50.2%, and with the introduction of ammonium nitrate is 80.75%), and soluble K_{SO3} increased by 18% (in acidic product K_{SO3} reaches 7.74%) apparently due to increased solubility of calcium sulfate. And the increase in sulfuric acid to this system from 2.3% to 3.49-4.84% SO_3 raises K_p respectively, up to 82.2-89.72% (2.9%). In the process of ammonization of the pulp to pH 3,2 water-soluble sulfates due to conversion is additionally increased by 7-13%, apparently due to metabolic processes:

$$CaSO_4+2NH_4H_2PO_4 \rightarrow Ca(H_2PO_4)_2+(NH_4)_2SO_4 \quad (3)$$

and depends on the degree of ammonization and the initial sulfate content (i.e., when replacing EPA with sulfuric acid by 10-20%, respectively). When drying product K_p increases by 5-10%.

With an increase in the concentration of the starting EPA to 25-35% P_2O_5 and when replacing 10-20% of its sulfuric acid K_p falls on 3-5% (K_p=74-82%) in acidic pulp, and in the dried product due to before decomposition are almost equal (K_p=92-94%) with K_p products obtained using the original 20% EPA. When replacing 20% EPA with sulfuric acid using EPA concentration 25% P_2O_5 where, K_{SO3}=69-7%). And with increasing the pH of the solution to 3-3,5% K_{SO3} rises to 73-80%. However, K_p phosphorus, respectively, drops to 60-32% (in EPA concentration 25%, K_p=70%). This can be explained by the fact that with the introduction of ammonium nitrate into EPA, the solubility of calcium sulfate crystals apparently increases and has a certain value (which we are studying) and depends on the concentration of both phosphoric and sulfuric acid in the solution. Apparently, this factor also affects the process proceeding according to equation 3 during the ammonization of acidic pulp. In addition, ammonia is not enough to completely complete the process proceeding according to equation 3.

Increasing neutralization (pH) of acidic pulp with ammonia, the degree of decomposition of phosphorite and the degree of conversion of sulfates are opposite. So with increasing pH of the solution K_p phosphorite falls and K_{SO3} sulfates rises. In addition, the fact that K_p phosphorite when using weak ammonium nitrate activated (20% P_2O_5) EPA with a partial 20% replacement by sulfuric acid (pH about 1) ammoniated (pH about 2) pulps and in the product (pH about 2) are close to K_p phosphorite in the same products when it is processed using activated and evaporated EPA for a concentration of 25-35% P_2O_5 and containing as much sulfuric acid. So, K_p under these conditions it is in the range of 89-82% in acidic pulp, 80-83% in ammoniated pulp (pH about 2) and 84-90% in solid product (pH about 2) However, water-soluble sulfates are low (65-80%) in finished product. Therefore, when choosing sulfates are low (65-80%) in the finished product. Therefore, when choosing the optimal technological parameters, these opposite processes must be taken into account.

We recommend the following optimal conditions for the production technology of a new type of sulfoammophos fertilizer with the introduction of ammonium nitrate phosphate in the process of decomposition according to the above equation:

a) for non-evaporation EPC systems: use of weak (about 21% P_2O_5) EPC it is necessary to establish the weight ratio of the starting components: EPC (100% P_2O_5):H_2SO_4: phosphorite = 1,3:0,2:1,0; process temperature t_p= 60° C; decomposition time $\tau = 2$ hours; the degree of neutralization of the pH of about 2; drying temperature t_c= 105°C. In this process, granulation and drying produce the process of evaporation of the pulp. Since the pulp contains 45-50% moisture. As a result, K_p reaches 90-75% K_{SO3}= 88-65% correspondingly.

This gives the product composition, in bulk % $P_2O_{5общ}$=48,0; $P_2O_{5усв}$=47,3; $P_2O_{5в.р.}$= 43,2; N=3, SO_{3tot}= 5,6; $SO_{3time.}$=5,0. Raising the pH to 2.5 reduces K_p phosphorite up to 70% and increases K_{SO3} till 95%. When choosing the above conditions for the release of the product, production and agrochemical needs are taken into account;

b) the following process parameters are optimal for an evaporated EPC system: concentration of activated EPC 30-35% P2O5; EPC weight ratio (100% P_2O_5):H_2SO_4: phosphorite = 1,3:0,2:1,0, t_p=60° C, τ_{others}= 2 hours, solution pH about 2; t_e=105°C.

As a result, K_p phosphorite reaches up to 88-90%, where K_{SO3}=68-72%. In this case, the process of evaporation of the pulp is not performed, since the ammoniated pulp contains 37-27% moisture, depending on the concentration of the initial EPA. In order to protect the environment from fluoride emission when using bubbling evaporation, it is necessary to evaporate EPA to a concentration 28% P_2O_5. Get the product composition, in mass. % P_2O_{5tot} = 44-45; $P_2O_{5\ assimilation}$ =44,0-44,2; $P_2O_{5\ time.}$ = 37,0-37,5; N = 2.5-3.0; SO_{3total}=6,3-6,7.

Fertilizers obtained according to both options incorporate mono- and diphosphate of calcium, magnesium, monophosphate, ammonium nitrate and sulfate, calcium sulfate, etc.

Thus, in the course of the study, the preparation of calcium-containing nitrogen-phosphorus fertilizer with soluble sulfates established that in the process of decomposition of magnesium-containing phosphorites of Karatau, at a weight ratio of EPA ($100\%P_2O_5$) phosphorite = 1,5:1,0 at a temperature 60^oC within 2 hours, in the activated EPA of ammonium nitrate, the degree of decomposition of the raw material is significantly (20-25%) increased compared to the use of EPA without ammonium nitrate and depends little on the initial concentration (20-35% P_2O_5) EPA (K_p phosphorite in the pulp is about 75%): an increase in sulfuric acid in the original EPA (20-35% P_2O_5) from 2.5 to 5-11% (SO_3) leads to increase K_p another 10-15% and is optimal. It should be borne in mind that when decomposing phosphorite in a weak (20-35% P_2O_5) EPC Content SO_{3total} should be in the range of 4.5-5.0%, in the pulp SO_{3total} = 2,7-3,0% K_p in the acid product is 88-92%, and in the ammoniated pH 2 K_p = 80-89% and water soluble sulfates K_{SO3}=87-88%.

With an increase in the concentration of EPA to 30-35%, the content SO_{3total} can be brought up to 11-11.5%. Wherein K_p in an acidic product it is equal to 92-93%, and in an ammoniated product up to pH about 2 K_p = 89-90%, K_{SO3}68-72%.

When neutralizing acidic pulp with ammonia, calcium sulfate is converted to ammonium sulfate, so the product increases the water-soluble plant nutrient for plants. Ammonium nitrate increasing the solubility of calcium sulfate, accelerates i.e. favors the conversion process. With increasing pulp pH to 2-2,5 K_p phosphorite is reduced to 85-70%, and when drying product K_p increases by 3-5%. Water-soluble sulfates 65-95% SO_3.

Thus, the process of phosphoric acid decomposition of secondary phosphate can be carried out with unpaired (21% P_2O_5) activated nitrate ammonium phosphate containing 4.5-5% sulfuric acid. And according to the evaporation EPC system with the use of a bubbler evaporator, in order to protect the environment from fluorite gases, it is necessary to evaporate EPC to a concentration of about 28% P2O5 and the sulfuric acid content can be brought up to 10-11%. Moreover, the degree of defluorination is below 5% and corresponds to the MPC.

Compared to the production of ammophos using a new technology in the production of phosphate 15-17%, the coefficient of sulfuric acid use increases by another 10%, since the feed pulp contains about 2.75% (according to our balance). This acid (free) is involved in the decomposition of secondary phosphate and in the conversion of calcium sulfate to ammonium sulfate in the process of pulp ammonization.

The latter switches to a water-soluble ammonium sulfate compound (about 65-95%, depending on the conditions of the ammonization process). In addition, phosphogypsum emissions are reduced by 21-23% (of which 15-17% due to phosphoric acid decomposition and 6% in the process of filtering EP, i.e., when some EP is introduced into EPA or when sulfuric acid is added to EPA before the process decomposition of phosphorite). Ammonia consumption will decrease by 70-80%.

III. CONCLUSION

Consequently, it was found that: during phosphorus-sulfuric acid decomposition of secondary phosphate (21% EPC is used P_2O_5 and 30-35%P_2O_5) optimal are the weight ratio of EPA ($100\%P_2O_5$): H_2SO_4 : phosphorite = 1,3:0,2:1,0, temperature 60 ° C, decomposition time 2 hours, ammonization at 80 ° C to a pH of about 2, drying at 105^oC. Get NPS fertilizer containing P_2O_{5total}=44-45%, $P_2O_{5\ assimilation}$ =4,00-44,2%, P_2O_{5time}=37,0-37,5%, N=2,5-3,0%, SO_{3total}=9,0-9,3%, SO_{3time}=6,3-6,7% and others K_p=88-90%, where K_{SO3} = 68-72%. At the same time, the consumption per unit of output is reduced by sulfuric acid by 15-25% for ammonia by 60-70%, the cost is reduced by 20-25%.

REFERENCES

1. Gafurov K. DE fluorination of fertilizers from Karatau phosphorites. Tashkent: Fan, 1992.
2. Shamshidinov I.T. Development of an improved technology for the production of extraction phosphoric acid and the production of concentrated phosphorus-containing fertilizers from phosphorites of Karatau and Central Kyzylkum: Abstract,dis,. doctor. tech. sciences. - Tashkent, 2017.- 66 p.