OPTIMIZATION OF CALCIUM NITRATE CONVERSION STAGE IN COMPLEX FERTILIZER PRODUCTION

Seitmagzimova G.[1], Issabayeva L.[1], Petropavlovsky I.[2], Seitmagzimov A.[1]

[1]M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan
[2]D.I. Mendeleyev Russian Chemical-technological University, Moscow, Russia

Email: galinaseit@mail.ru

ABSTRACT

Calcium nitrate conversion stage in azophoska production is connected with supersaturated solution formation causing small calcium sulphate crystallization. This complicates the process of precipitate filtration, washing and drying and increases the content of calcium ions in the conversion solution of potassium nitrate. The presented paper shows the results of investigation of calcium nitrate conversion with potassium sulphate solution to determine optimal conditions of the process and to provide maximal conversion degree. The results of the conversion investigation allowed to conclude that conducting the calcium nitrate conversion in 2 step mode with 80% pre-conversion and the following post-conversion to 20% excess of the precipitant promotes to reduce essentially supersaturation degree in initial mix. It provides to precipitate larger calcium sulphate crystals and to intensify significantly the suspension filtration process in NPK fertilizer production.

Key words**:** azophoska production, freezing-out calcium nitrate tetrahydrate, calcium nitrate conversion, filtration productivity, crystal average diameter, supersaturation.

INTRODUCTION

Presently mineral fertilizers production is one of the priority directions of development of the chemical industry of the Republic of Kazakhstan. Complex fertilizers are the most promising ones due to high concentration of N, P, K nutrients and the absence of ballast components. Azophoska is effective highly concentrated ternary fertilizer consisting of 3 main components: nitrogen, phosphorus and potassium [1]. This production based on phosphate rock nitric-acid decomposition allows to perform the process by wasteless technology with complex usage of all components of phosphate raw materials. The process includes insoluble residue separation from nitric-acid extract, the extract cooling with freezing-out calcium nitrate tetrahydrate, precipitate $Ca(NO_3)_2 \cdot 4H_2O$ separation, its washing, ammoniation and drying of nitrogen-phosphate solution, introduction of potassium component and granulation and drying NPK fertilizer [2].

The stage of calcium nitrate conversion is connected with supersaturated solution formation causing small calcium sulphate crystallization. This complicates the process of precipitate filtration, washing and drying and increases the content of calcium ions in the conversion solution of potassium nitrate. Therefore this stage slows down the process of NPK fertilizer production as a whole [3].

In real industrial conditions the ammonium carbonate solution is used for the conversion. Some scientists developed new methods of this conversion performance using ammonium sulphate and potassium carbonate as precipitators [4-6]. At the same time according to the recent data the EuroChem-Fertilizer (Kazakhstan) enterprise starts nowadays development of new potassium sulphate and complex mineral fertilizer productions in South Kazakhstan region. In this context substitution of ammonium-carbonate conversion into potassium sulphate application is a very relevant issue today. The presented paper shows the results of investigation of calcium nitrate conversion with potassium sulphate solution to determine optimal conditions of the process and to provide maximal conversion degree.

MATERIALS AND METHODS

To study the process of calcium nitrate conversion we used saturated potassium sulphate solution, containing 20% of K_2SO_4, and chemically pure calcium nitrate tetrahydrate. The process was performed at constant temperature 60ºC and stirring in a thermostat by calcium nitrate addition to the solution. The process was conducted for 2 hours. The time to reach the equilibrium equal to 2 hours was pre-determined. To establish the solution supersaturation degree we have studied the process of partial conversion with different potassium sulphate precipitant norm from stoichiometric consumption changing it from 60 to 120%. Simultaneously the influence of the conversion mode on the formed suspension filtration productivity and an average crystal size was determined. The filtration process was carried out at the laboratory filtration vacuum plant under vacuum 0.02 MPa. The filtration productivity ($kg/m^2 \cdot h$) by the wet precipitate was calculated by the standard method as a ratio of precipitate mass and a product of the filtration surface square and the process time. An average crystal size was determined at the photo sediment meter FSCh-6 with simultaneous definition of sample specific surface and particle size distribution. CaO content in the solution was analyzed by the standard method of complexometric titration.

At the second step partially converted calcium nitrate for every sample in the first stage was subjected to further conversion up to 120% norm of potassium sulphate. The same analyses were carried out at that.

RESULTS AND DISCUSSION

Research results are reflected in Figures 1-6. Supersaturation degree C/C_0 was calculated for each precipitant consumption for the conversion. To describe the process of calcium sulphate crystallization the determination of CaO content in liquid phase after the conversion is the most reliable analysis. As it shows the most part of calcium oxide is gradually precipitated at K_2SO_4 norm interval 40-70% (Fig. 1, curve 1); at that intensive crystal formation takes place and small amount of solid phase is precipitated because of relatively small suspension supersaturation.

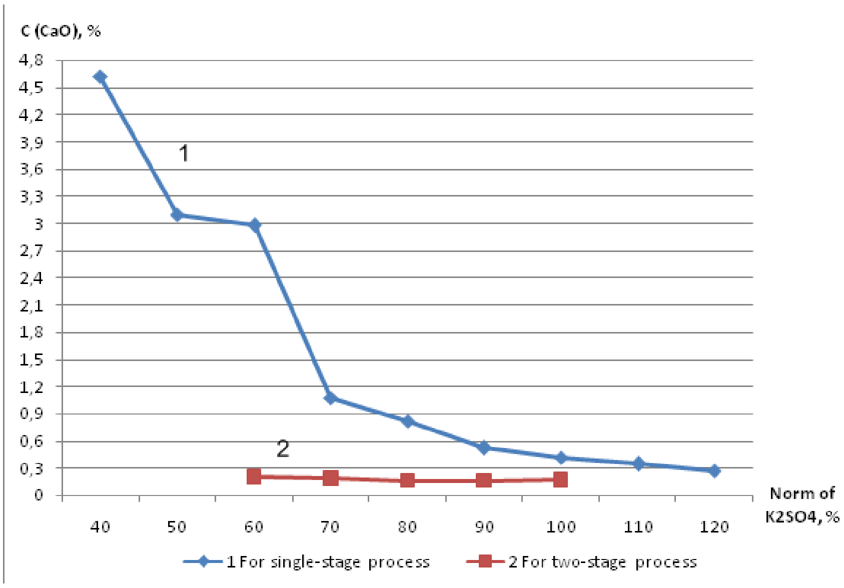

Fig. 1. Dependence of CaO content in a conversion solution on potassium sulphate solution norm

In a case of norm change from stoichiometric amount to 20% excess of potassium sulphate the crystallization process takes place from solutions with high supersaturation, and precipitation proceeds approximately completely keeping some small supersaturation. Fig. 1 (curve 2) shows also that when the conversion takes place in 2-step mode, less by 35-40% value of CaO content in the liquid phase is reached comparing to 1-step partial conversion – 0.161% versus 0.266%. It is explained by formation of the system with less supersaturation at the first step conversion, from which maximum CaO is precipitated as calcium sulphate and the stable equilibrium solution of potassium nitrate is formed. Calcium oxide content in this solution corresponds to the solubility in this system.

It is known that high supersaturation degree of water solutions has the determining value on the size of formed crystals. That's why we have studied the influence of the precipitant consumption for partial 60-120% conversion on the crystal size and on precipitate filtering properties. These dependences are presented in Figures 2 and 3. Fig. 3 (curve 1) shows that relatively small calcium sulphate crystals are formed at potassium sulphate consumption change in the interval 40-80% of stoichiometric amount; the filtration productivity by the wet precipitate has low values in these conversion conditions as well Fig. 2 (curve 1). It is connected with lack of the precipitant causing crystallization of small amount of precipitate particles which are capable to the further increase in size and can be the seed for crystal growth. Further precipitant norm increase from 80 to 100% causes some calcium sulphate crystal growth from 47.2 to 61.0 micrometers and hence suspension filterability increase from 50.3 to 74.2 $kg/m^2 \cdot h$. In this case it is enough material for forming larger crystals. Reduction of these indicators at 20% excess of the precipitator is due to the creation of very high supersaturation and correspondingly high crystallization rate. So, these data prove that the ratio of rates of nucleus formation and crystal growth is the determining factor for precipitate particle size. In turn this size predetermines formed suspension filtration properties.

To establish optimal conditions of calcium nitrate conversion from the point of view of system supersaturation degree the partial and complete conversion was studied.

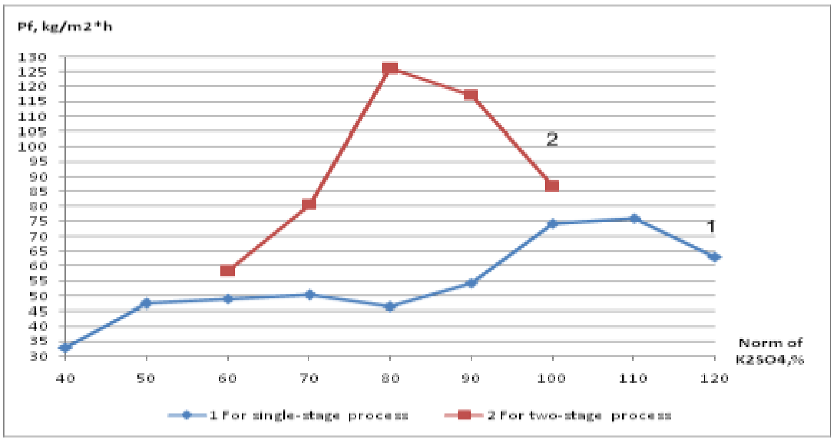

Fig. 2. Conversion mode influence on suspension filtration productivity

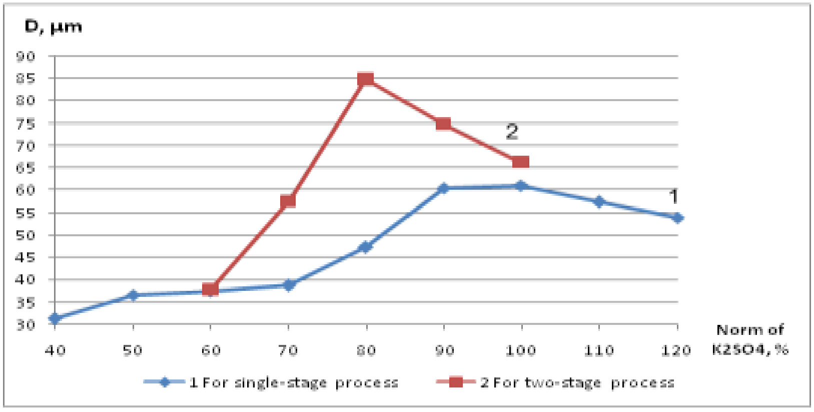

Fig. 3. Conversion mode influence on average diameter of calcium sulphate particles

We offer 2-step calcium nitrate conversion to obtain large crystals of calcium sulphate precipitate and to improve suspension filterability. It includes feeding a part of potassium sulphate solution for the first step and form suspension treatment with the rest amount of the precipitant. It was determined that essential increase of initial solution supersaturation takes place at 10-20% excess of precipitant stoichiometric amount. Just at this supersaturation degree the particle size decrease from 61 to 54 micrometers is observed (Fig. 4).

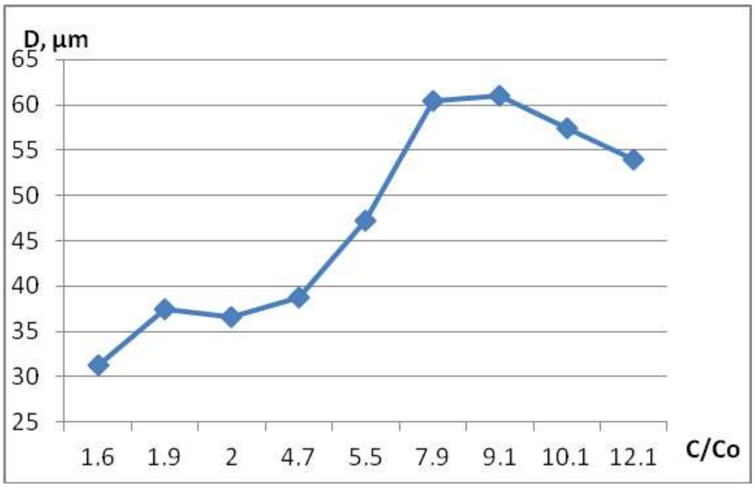

Fig. 4. Dependence of size of calcium sulphate particles on solution supersaturation degree at 1-step conversion

It allows to determine the optimal condition of conversion first step corresponding to 90-100% of K_2SO_4 norm for the conversion. At this mode solution supersaturation is markedly reduced with simultaneous separation of sufficient amount of solid phase, which can serve as a seed for the second stage. For complete calcium sulphate precipitation the obtained suspension is subjected to treatment with the rest amount of the precipitant. In this case some amount of calcium sulphate is used as a seed; on its surface the rest amount of this compound is precipitated, and the crystal is growing around all its faces. At the second step less supersaturated solutions are formed; small crystals are formed in the case of 60% 1-step conversion because of viscous concentrated solution formation with supersaturation degree 15.2 and absence of excessive material for particle coarsening (Fig. 5).

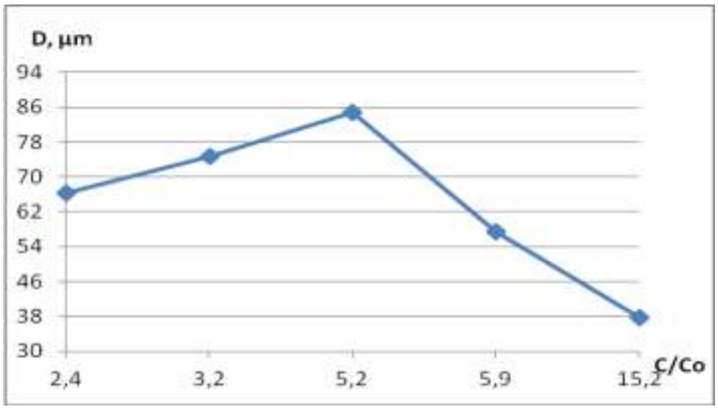

Fig. 5. Dependence of size of calcium sulphate particles on solution supersaturation degree at 2-step conversion

Studying the conversion second stage in the interval 60-100% norm of potassium sulphate solution revealed that at any norm higher values of filtration productivity and crystal average size are reached (Fig. 2 and 3 (curves 2)). After suspension post-treatment at the second stage up to the complete conversion these dependences pass through a maximum at 80% norm at the 1 step. Hereat the filtration productivity has considerably large value 126.01

kg/m^2·h comparing to the direct conversion 46.55 kg/m^2·h. Correspondently post-treatment of the suspension containing $CaSO_4$ seed crystals of 47.2 micrometers (formed at the partial conversion) results in increasing crystal average size up to 84.8 micrometers, i.e. by ~80% due to growth on the available solid surface at 80% initial norm. At a lack of a seeding surface for fast supersaturation removal the additional amount of new nuclei is formed; it causes average diameter decrease to 38 micrometers like at the partial conversion.

Verification of experimental results on the calcium nitrate obtained by freezing-out calcium nitrate tetrahydrate has shown similar results of increasing the crystal average diameter at 2 step conversion comparing to the direct conversion from 42.1 to 71.3 micrometers, i.e. by 70% (Fig. 6). The filtration productivity by a wet precipitate has the same trend to increase from 70.46 to 99.92 kg/m^2·h at transition from direct to 2-step conversion (Fig. 7).

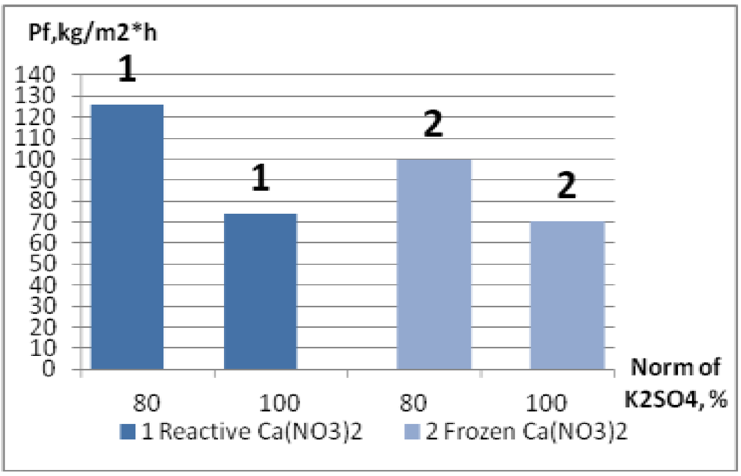

Fig. 6. Comparison of precipitate average diameter obtained from reactive (1) and frozen out calcium nitrate (2)

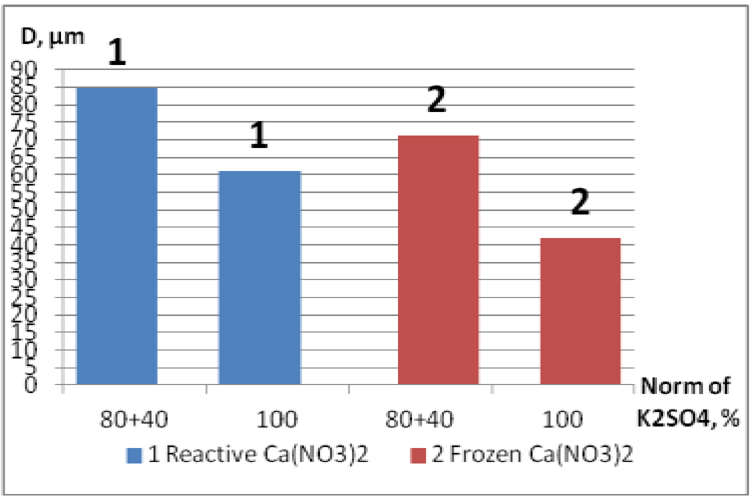

Fig. 7. Comparison of filtration productivity for suspension obtained from reactive (1) and frozen out calcium nitrate (2)

Relatively low diameter and filtration productivity values comparing to reactive salt conversion is caused with the influence of impurities in the composition of calcium nitrate frozen out of nitric-acid extract. The impurities cause change in shape and size of the gypsum crystals and the formation of more dense precipitate packing which deteriorates of suspension filtration.

CONCLUSION

Obtain results of the conversion investigation allow to conclude that conducting the calcium nitrate conversion in 2 step mode with 80% pre-conversion and the following post-conversion to 20% excess of the precipitant allows to reduce essentially supersaturation degree in initial mix and to precipitate larger calcium sulphate crystals with best filtration properties. The performed analysis of conversion mode influence on calcium sulphate crystals formation from supersaturated conversion solutions proved the significant effect of initial solution supersaturation degree on the crystal size at the first step of conversion and of seed crystals size and its amount at the second step. Performance of calcium nitrate conversion in optimal mode with 80% of precipitant norm feed to the first stage and the rest amount of potassium sulphate to 120% of stoichiometric amount for rest calcium ions precipitation promotes to increase particle average size by 70-80% and to filtration productivity twofold. It allows to precipitate more uniform $CaSO_4$ large crystals and to intensify significantly the suspension filtration process which is the limiting stage in azophoska production.

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