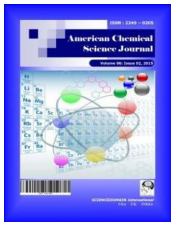

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Conversion of Calcium Nitrate Solution Obtained from Kyzylkum Phosphorite with Ammonium Carbonate

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Authors' contributions

This work was carried out in collaboration between all authors. Author AJA designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors AUE and AMR managed the analyses of the study. Author AJA managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The effect of the concentration of the amount of ammonium and calcium nitrate, the ratio of ammonia and nitrate nitrogen in the solution on the process of conversion of calcium nitrate formed during the processing of low-grade phosphorite with nitric acid has been studied. It has been shown that increasing the ratio of ammonia nitrogen to nitrate and concentrations of amount salt in the initial solution of ammonium and calcium nitrate promotes the process of conversion of calcium nitrate into calcium carbonate and ammonium nitrate.
It has been studied that the effect of various process parameters on the process of filtration and sedimentation of calcium carbonate's sediments. Under optimum conditions, the filtration rate of the resulting calcium carbonate is 2-3 t/(m^2 h) in wet cake.

Keywords: Calcium and ammonium nitrate's solution; ammonium carbonate; conversion; filtration; sedimentation of calcium carbonate.

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1. INTRODUCTION

In modern conditions, the use of mineral fertilizers (nitrogen, phosphate and potash) is a decisive factor for obtaining high yields of crops in agriculture. Therefore, provision of agricultural by fertilizers in all parts of the world is highlight in solving the food problem.

Uzbekistan has a large branch of the chemical industry, which is working on agriculture. In 2015, the chemical industry enterprises produced 942.72 thousand tons of nitrogen, 148.42 thousand tons of phosphorus and 143.24 thousand tons of potassium. Annual the demand of the republic is 839.58 thousand tons of N, 525.21 thousand tons of P_2O_5 and 278.92 thousand tons of K_2O in the form of fertilizer based on 100% of the nutrients. It should be noted that in the near future production capacities of Dehkanabad complex of potassium fertilizers will be 360 thousand tons of K_2O per year and demand of agriculture will be satisfied not only by nitrogen fertilizers, but also potassium.

In a complicated manner is the case with phosphate fertilizers. It is known that industry meets the need of agriculture in phosphorus fertilizers is only by 27%. However, Kyzylkum phosphorite complex is not able to provide our plants with cheap and high-quality raw materials. It produces phosphorites from Central Kyzylkum deposit Republic of Uzbekistan, exposes them to crushing and classification, produces washing them from chlorine and calcining to decompose the carbonates and remove carbon dioxide. Mineralized mass (12-14% P_2O_5) and a phosphorite slurry (8-10% $P_2O_{5)}$ are stored in the slime reservoir as the production of waste at the plant. In connection with acute shortage of phosphate raw materials should be involved these sources of phosphorous in the production of phosphate fertilizers.

The second is very actual problem that connected with a single phosphate fertilizers production. The fact, that all our plants produce nitrogen-phosphate fertilizer. However, they cannot be used under the autumn plowing. Contain nitrogen in it is washed away to the spring sowing by rainfall and melt water from the soil. Phosphate fertilizers are most effective under the deep autumn plowing. Thus, under cotton is required 60-70% of the annual application norms, phosphate fertilizers need to make under the autumn plowing and under the grain crops is 100%. In according with the areas on which is grown cotton and grain, the need of agriculture in the single phosphorus fertilizers is 272 - 292 thousand tons of P_2O_5 per year. At present, a simple ammoniated superphosphate can be accepted with stretching to single-phosphorus fertilizer (1.5% N and 13.5% P_2O_5). However, it is made very little (22.9 thousand tons of P_2O_5 per year).

The acute shortage of phosphate fertilizers, due to the limited amount of high-quality phosphate rock, it is necessary to find alternative methods of processing phosphate from Central Kyzylkum. As analysis of scientific and technical literature and manufacturing practices of chemical plants of the republic by the acid processing of phosphorite Central Kyzylkum on phosphate concentrate, wet processing phosphoric acid (WPA) and phosphorus fertilizer shown that obtained results are not sufficient for the successful expansion of the production processes of the above products in the industrial scale.

One of these difficulties is the high calcium module (1.9-2.8) and the presence of chlorine in the reaction medium. Based on calculations it is shown that the reduction of calcium module up to 0.1 leads a reduction of acid reagent consumption and emitted heat amounts 7-8 and 10-15%, respectively [1]. Therefore, when the acid processing of low-grade phosphate rock should be noted the task of lowering calcium module of phosphate rock with acid-free manner.

Hence we [2,3] investigated processing high calcareous phosphate by circulating ammonium and calcium nitrate solution (CACNS) with a total content of 20-50% salt, at a ratio of ammonia nitrogen to nitrate nitrogen (N_{amm}-ammonium nitrogen and $N_{nit.}$ - nitrate nitrogen) is within 0.20-0.80. At the same time it is determined that the outlet of P_2O_5 in the concentrate is 55-65% of the calcium module value is reduced by 0.18-0.56 relative to the initial. The dried and washed concentrate depending on the conditions of experiments contains 18.27-19.60% of $P_2O_5$and 44.66-48.42% of CaO. Along with washed concentrate in the technological cycle at the same time got suspended liquid fertilizer containing 2-4% P_2O_5 and 12-14% N.

We have also studied the process of ammoniation of nitric acid extract obtained by decomposition of the pretreated phosphate rock by CACNS and technological research was carried out the process of obtaining phosphorus

and suspended liquid fertilizer from nitric acid extract ammoniation products Central Kyzylkum phosphate [4]. These laboratory experiments have shown the possibility of processing high calcareous Central Kyzylkum phosphorites for concentrated phosphoric and liquid complex fertilizers. A resource-saving technological scheme was proposed and material balance of production was calculated.

It should be noted that when the recycled slurry and ammoniation of the nitric acid extracts during the nitric acid decomposition phosphate pretreated slurry is formed, consisting of solutions of ammonium nitrate and calcium (NAC) and a precipitate. The first part of the filtrate, formed during the precipitate separation is returned to the stage of nitric acid recycled slurry as CSACN. The second part of the NAC solution can be processed using various approaches:

1. The immediate evaporation of the solution for obtaining nitrogen-calcium fertilizers leads to a product with worsened physical and chemical properties.
2. Conversion of calcium nitrate by ammonium carbonate solution or ammonia gas and carbon dioxide to produce ammonium nitrate and calcium carbonate proceeds according to the following equation:

$$Ca(NO_3)_2 + (NH_4)_2CO_3 = CaCO_3 + 2NH_4NO_3$$

After separating the sludge filtrate containing ammonium nitrate, it is sent to the pre-treatment of low-grade phosphate rock as CACNS. Filtered and washed chalk can be used as a building material or a high-performance means for liming of soils.

In this connection, we have investigated the process of obtaining calcium carbonate and the effect of the amount of concentration of NAC (30-50%) and the ratio (N_{amm}: N_{nit}= 0: 1-1: 0) on the process of conversion of calcium nitrate to the second way. It should be noted that in the literature [5,6] studied 29-33% solution of calcium nitrate solution or a mixture of calcium and ammonium nitrate at a ratio N_{amm}: N_{nit} = 0: 1, 1: 1. In our conditions, the amount salt content reaches to 60%, and the ratio of N_{amm} : N_{nit} ranges from 0: 1 to 1: 0 (0: 1; 0.2: 0.8, 0.4: 0.6, 0.6 : 0.4, 0.8: 0.2, 1: 0).

2. EXPERIMENTS

Laboratory facility consisted of a 0.5-liter reactor equipped with a stirrer rotating at a speed of 300-500 rpm and heat exchange jackets to maintain the process temperature. The reactor was charged with a solution of NAC, and within 5 minutes, a calculated quantity of ammonium carbonate.

When analyzing the isotherm charts Ca^{2+}, NH_4^+ // $2NO_3^-$, CO_3^{2-} - H_2O set ratio of the starting components is $\frac{Ca(NO_4)_2}{(NH_4)_2CO_3} \leq 1$ and at 30-60^{0}C. In this regard, experiments were conducted at $\frac{Ca(NO_4)_2}{(NH_4)_2CO_3} = 1$. The duration of the process was 60 minutes.

The resulting slurry was filtered under vacuum at 0.5 kg / cm^2 on a Buchner funnel through a layer of filter paper Whatman. Calculation filtering efficiency is performed according to the formula:

$$v = \frac{m}{S \cdot t}$$

where,

V is filtration rate, kg / m^{2}h,
m is mass of the wet precipitate, t;
S is area of filtered surface, m^2;
t is the filtration time, hour [7].

Calcium carbonate precipitate is washed with water at the rate of 18 g water to 16 g of dry residue. The resulting precipitate was dried at 100-105°C and analyzed by the known technique [8]. Ammonium and nitrate nitrogen content were determined by sublimation (method of Kjeldahl). CaO is defined by of complexometric titration of 0.05 N solution of EDTA in the presence of calcein indicators.

Ratio of N_{amm}: N_{nit} and the amount salt concentration was varied in the range of 0.4: 0.6 - 0.8: 0.6 and 30-60% respectively. During the experiments the estimated amount of ammonium carbonate was kept constant - 110% of the stoichiometry for the maintenance of calcium nitrate in the initial solution. The temperature was maintained in the range 60-65℃. The results are shown in the Table 1.

3. RESULTS AND DISCUSSION

As can be seen from the Table 1, the pH of the solutions and the ratio S: L, depending on the ratio of N_{amm} : N_{nit} and concentrations of salts amount varied between 7.22-8.30 and 1: 4.4-1:

8.0 respectively. Increasing the ratio of N_{amm} : N_{nit} and concentration of salts in the initial solution, the amount of NAC, promotes significant intensification of conversion processes of calcium nitrate in calcium carbonate and ammonium nitrate. Increasing the value of conversion degree allows increasing the concentration of ammonium nitrate in the obtained solution from 30 to 70%, which compares profitably with existing methods [9].

With increasing ratio of N_{amm}: N_{nit} and S:L (it is ratio of solid phase to liquid phase) in the suspensions reduced from 1: 4.4 to 1: 8. Application filtering method for the separation of such a suspension is not justified. Therefore, further research we studied the effect of process parameters on the process of sedimentation and filtration of calcium carbonate precipitation. The Fig. 1 shows that within 30 minutes the degree of lightening is 68%, and after 50 minutes at -78% N_{amm}: N_{nit} = 0.8-0.2 and amount salt concentration is 50% with a decrease of N_{amm}: N_{nit} to 0.6- 0.4 in the same conditions, the degree of lightening is 22 and 36%. This is due to the fact that increasing concentrations of amount salt in the original solution NAC from 30 to 50% when N_{amm}: N_{nit} = 0.6: 0.4 leads to reduce deposition rate 0.091 m / h to 0,039 m / h. With increasing N_{amm}: N_{nit} 0.6: 0.4 to 0.8: 0.2 increased sedimentation rate 0.039 m/h to 0,105 m/h, that is, 2.69 times.

There has been also investigated the influence of the ratio S: L in the filtration speed of calcium carbonate. As shown by the experimental data with the increase of S: L to 1: 2.3 while other parameters are constant filtration rate increases 1.2-3 times. Therefore, the application of NAC with a ratio of N_{amm}: N_{nit} more than 0.8: 0.2 with calcium carbonate before filtration separation is desirable to install precipitation tanks are available to reduce the ratio of S:L in 3 times.

Filtration efficiency of calcium carbonate precipitate obtained is 3.2 t/(m^2 h) in a wet cake. Precipitation humidity depending on process parameters range from 28.28 to 59.31 wt. %. The resulting conversion of calcium nitrate (which is part of the NAC) solution of ammonium nitrate could be recycled for ammonium nitrate fertilizer suspended nitrogen-phosphorus calcium fertilizer.

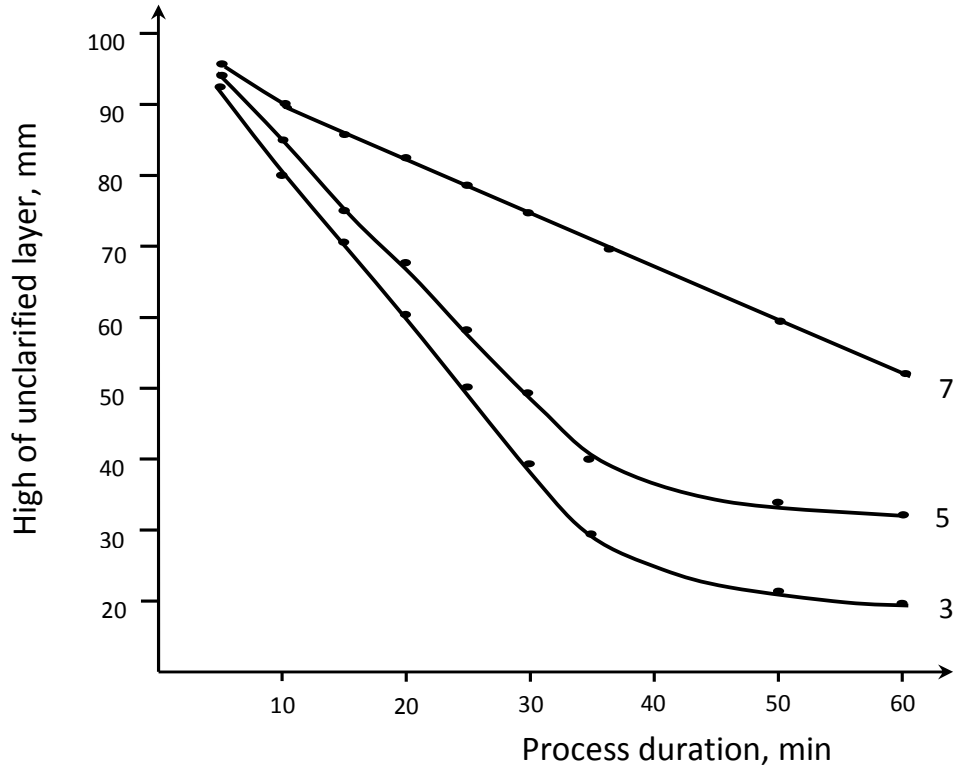

Fig. 1. The dependence of the height of the unclarified suspension layer on the duration of the sediment. The curves norm corresponds to numbers of the table

Table 1. The effect of various technological parameters on the calcium nitrate conversion process

№ experiments	N_{amm}: N_{nit}	Salt concentr-ation, %	pH solution	Height of wet $CaCO_3$, mm	Filtration speed of the wet $CaCO_3$ after conversing, $t/m^2 \cdot h$	Filtration speed during the washing, $t/m^2 \cdot h$	Moisture of remain mass., %	CaO in the filtrate, %	Density of filtrate, g/cm^3	Ratio of S:L	Conversion degree %
1		30	7.87	6.5	3.0	3.76	47.02	0.02	1.094	1:8.0	99.7
2	0.8:0.2	40	7.79	5.5	2.88	3.70	43.26	0.02	1.136	1:6.4	99.6
3		50	7.73	5.5	2.76	3.64	35.53	0.01	1.185	1:5.3	99.6
4		60	7.71	5.0	2.55	3.64	28.28	0.03	1.249	1:4.7	98.5
5		30	8.12	10.0	2.91	3.70	53.76	0.028	1.108	1:7.8	99.5
6	0.6:0.4	40	8.21	10.0	2.80	3.65	46.93	0.042	1.153	1:6.2	99.0
7		50	8.23	7.0	2.69	3.59	38.46	0.040	1.203	1:5.0	98.7
8		60	8.27	7.0	2.53	3.50	30.05	0.044	1.258	1:4.5	98.5
9		30	8.31	8.0	2.75	3.55	59.31	0.070	1.115	1:7.5	99.5
10	0.4:0.6	40	8.30	8.0	2.70	3.47	50.4	0.077	1.174	1:6.0	99.3
11		50	7.96	8.0	2.61	3.40	48.8	0.084	1.210	1:4.7	98.5
12		60	7.22	9.0	2.2	3.3	32.0	0.011	1.300	1:4.4	98.4

The chemical composition of calcium carbonate produced during the conversion of calcium nitrate corresponds fully meets to State standard "Chemically precipitated chalk" and it can be used as filler, a building material or a highly effective means for liming of soils.

4. CONCLUSION

There has been studied that effect of the ratio N_{amm}: N_{nit} and the concentration of ammonium nitrate and calcium solutions (NAC) on the techno-analytical indices of the calcium nitrate conversion. It is found that with increasing ratio of N_{amm}: N_{nit} from 0.4: 0.6 to 0.8-0.2 decrease the concentration of NAC and the degree of conversion of calcium nitrate and filtering efficiency, wet calcium carbonate increases from 80.0 to 99.9% and from 0.6 to 3 t/m^2 h, respectively.

On the basis of the experiments showed that the application of NAC with a ratio of N_{amm}: N_{nit} more than 0.8: 0.2 with calcium carbonate before filtration separation is to install sedimentation tanks are available to reduce the ratio of S: L in 3 times.

The resulting conversion of calcium nitrate, ammonium nitrate solution can be reprocessed to the ammonium nitrate fertilizer or suspended nitrogen-phosphate-calcium fertilizer. The chemical composition, resulting in the conversion of calcium nitrate formed calcium carbonate, correspond fully with the state standard "Chemically precipitated chalk" and it can be used as a filler, a building material or a highly effective means for liming of soils.

Thus, the industrial implementation of the process of conversion of calcium nitrate can solve most complex and topical problems when the preparation of nitrogen fertilizers and chemical calcium carbonate.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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