



NONCAKING AMMONIA NITRATE WITH THE ADDITION OF A SOLUTION OF NITRIC ACID DECOMPOSITION OF APATITE

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Annotation. The article shows that before adding apatite solution (RAP) to ammonium nitrate, apatite is first decomposed in a special reactor with the required amount of nitric acid. Then the resulting apatite-nitrate solution is separated from the insoluble residue by settling in a settling tank. Next, a nitric acid solution (AAS) of apatite containing 2.5-3.5% P_2O_5 is fed to the ITN (Use of Neutralization Heat) apparatus. There it is neutralized with gaseous ammonia to a slightly acidic reaction and mixed with a pure ammonium nitrate solution at a temperature of 175-1800C, evaporated in the first evaporation stage. At the last stage, the phosphate-nitrate melt (99.5%) was granulated by prilling in a granulating tower.

Keywords: ammonium nitrate, nitric acid extract, apatite decomposition solution, dicalcium and tricalcium phosphates.

NONQOTIRUVCHI AMMIYAKLI SELITRA APATITNING AZOT KISLOTASI BILAN PARCHALANISH ERITMASI QO'SHILGAN HOLDA

Annotatsiya Maqolada ammiakli selitra ishlab chiqarish jarayonida fosfat tarkibli eritmalar qo'llanilishi tahlil qilinadi. Apatit eritmasi (RAP) ammiakli selitrage qo'shilishidan avval, apatit maxsus reaktorda ma'lum miqdordagi azot kislotasi bilan parchalanadi. Keyin hosil bo'lgan apatit-nitrat eritmasi cho'ktirish idishida erimaydigan qoldiqlardan ajratiladi. Shundan so'ng, tarkibida 2,5-3,5% P_2O_5 bo'lgan apatitning azot kislotali eritmasi (AAS) ITN (neytrallash issiqligidan foydalanish) apparatiga yuboriladi. Bu yerda eritma gazsimon ammiak bilan neytrallanib, bir oz kislotali reaksiya hosil qiladi va 175-180°C haroratda toza ammiakli selitra eritmasi bilan aralashtiriladi hamda birinchi bug'lanish bosqichida bug'latiladi. Oxirgi bosqichda esa fosfat-nitrat eritmasi (99,5%) granulyatsiya minorasida purkash orqali granula shaklida hosil qilinadi.

Kalit so'zlar: ammiakli selitra, azot kislotasi ekstrakti, apatit parchalanish eritmasi, dikaltsiy va trikaltisiy fosfatlar.

НЕСЛЕЖИВАЮЩАЯСЯ АММИАЧНАЯ СЕЛИТРА С ДОБАВЛЕНИЕМ РАСТВОРА АЗОТНО-КИСЛОТНОГО РАЗЛОЖЕНИЯ АПАТИТА

Аннотация В статье рассматривается применение фосфатсодержащих растворов в процессе производства аммиачной селитры. Перед добавлением раствора апатита (RAP) в аммиачную селитру апатит сначала разлагается в специальном реакторе с необходимым количеством азотной кислоты. Затем полученный апатит-нитратный раствор отделяется от нерастворимого остатка путем отстаивания в отстойнике. Далее азотно-кислотный раствор апатита (AAS), содержащий 2,5-3,5% P_2O_5 , подается в аппарат ИТН (Использование Теплоты Нейтрализации). Здесь он нейтрализуется газообразным аммиаком до слабокислой реакции и смешивается с чистым раствором аммиачной селитры при температуре 175-180°C, испаряется на первой стадии испарения. На завершающем этапе фосфат-нитратный расплав (99,5%) гранулируется методом распыления в грануляционной башне.

Ключевые слова: аммиачная селитра, экстракт азотной кислоты, раствор разложения апатита, дикальций и трикальций фосфаты.

Introduction.

Ammonium nitrate is one of the most common and inexpensive nitrogen fertilizers used in agriculture [1]. However, it has two very serious drawbacks - caking and explosiveness [2]. To eliminate these drawbacks, various additives are added to AS.

The following are used as additives that reduce the level of potential danger of ammonium nitrate:

- carbonate-containing compounds of natural and man-made origin (chalk, calcium carbonate, dolomite);
- potassium-containing substances (potassium chloride, potassium sulfate);
- substances containing ammonium: ammonium sulfate, ammonium ortho- and polyphosphates;
- other ballast substances that do not carry a useful load, but determine only the mechanical dilution of ammonium nitrate (gypsum, phosphogypsum, etc.) [3].

Literature review. The addition of phosphate-containing solutions to **ammonium nitrate** is a subject of growing interest, as it enhances the **chemical stability** of the product and contributes to its agricultural effectiveness.

• **Martynov, A. et al. (2014)** conducted experiments on ammonium nitrate granulation with phosphate additives, concluding that phosphate presence significantly alters crystallization dynamics, reducing caking tendencies.

• **Chang, T. & Li, Z. (2017)** studied the role of phosphate impurities in ammonium nitrate solutions, reporting that phosphate integration results in better dispersion properties of the final product.

• **Bolshakov, I. et al. (2019)** investigated neutralization processes in nitrate-phosphate solutions, demonstrating that **controlled pH** adjustments can improve stability and granulation efficiency.

Research methodology. The additives of the first group are used in the production of the so-called calcium ammonium nitrate [4-6]. In Europe, it is produced by 31 companies, in Russia - five industrial enterprises. But its use is effective only on acidic European soils. On alkaline carbonate soils of Uzbekistan, it is ineffective. In addition, calcium ammonium nitrate in a powdered state is also explosive. Of the substances - additives of the second group, potassium chloride is widely used for the production of potassium ammonium nitrate. The latter is produced in foreign countries in fairly significant quantities with a content of 16-16.5% N and 25-28% K_2O [7]. But it is known that chlorine anions are catalysts for the decomposition of NH_4NO_3 . The presence of NH_4Cl in nitrate in an amount of 0.1% leads to its rapid decomposition at temperatures below $175^{\circ}C$. The introduction of potassium sulfate into the composition of AS is unlikely to be expected in the near future due to its high cost and small production volumes. Representatives of the fourth group of additives to ammonium nitrate are also promising: gypsum and phosphogypsum [8-12]. In these works, a technology was developed for obtaining a heat-stable fertilizer based on ammonium nitrate by introducing dihydrate, hemihydrate of phosphogypsum and natural gypsum into its melt. The resulting product with a 5% additive of phosphohemihydrate and containing 33.6% N had twice the strength of granules than pure nitrate, retained 100% friability for 4 months, withstood 7 thermal shifts at a temperature of $20 \leftrightarrow 60^{\circ}C$ without a significant decrease in the static strength of the granules, and had a weaker solubility compared to pure nitrate. The product had significantly higher thermal stability compared to pure ammonium nitrate (activation energy for pure nitrate was 160 kJ/mol; with the maximum amount of phosphogypsum additive it was 240 kJ/mol).

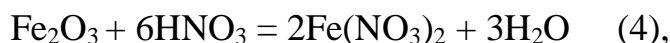
Results and analysis. The third group of additives are used at Cherepovets Azot OJSC, where in 2002 the production of stabilized ammonium nitrate of 32% N and 5% P_2O_5 was launched with a capacity of 400 thousand tons of fertilizer per year by introducing liquid complex fertilizer containing 11% N and 37% P_2O_5 and obtained from superphosphoric acid into the nitrate melt, i.e. an additive from a mixture of ammonium ortho- and polyphosphates was used. This additive increased the temperature of the onset of nitrate decomposition by $22-24^{\circ}C$, slowed down the rate of its thermal decomposition, increased the strength of the granules, reduced the porosity of the product, made the nitrate more resistant to repeated phase transformations, and most importantly, reduced the ability of the nitrate to detonate [13-16]. But superphosphoric acid is not produced in Uzbekistan. In addition, it is very expensive. The essence of the technology we offer is as follows: before adding the apatite solution (RAP) to the ammonium nitrate, the apatite concentrate is decomposed with the required amount of nitric acid in a special reactor. The resulting solution is separated from the insoluble residue in a settling tank. The reactor and settling tank operate continuously. Then the nitric acid solution (AAS) of apatite, containing 2,5-3,5% P_2O_5 , is pumped into a pressure tank or storage facility. From the pressure tank, the AAS of apatite is fed to the ITN apparatus, where it is neutralized with gaseous ammonia to a slightly acidic reaction. The resulting lyes are neutralized to a slightly alkaline reaction in a final neutralizer and mixed with a solution of pure ammonium

nitrate evaporated at the first evaporation stage. Then the phosphate-nitrate solution evaporates to 99.5% in the evaporator reactor and is transferred to the upper part of the granulation tower using a submersible pump, and from there the melt is sprayed into the lower part of the tower. After which the products are crushed and analyzed using known methods [17-19].

The process of decomposition of apatite by nitric acid can be represented by the equation:



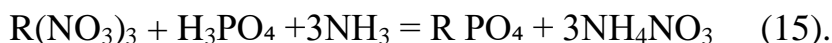
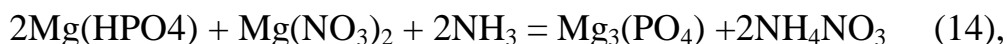
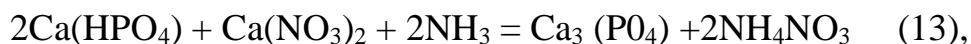
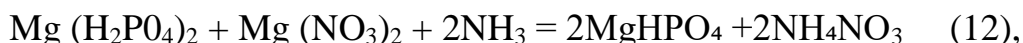
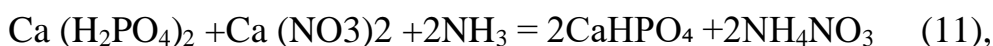
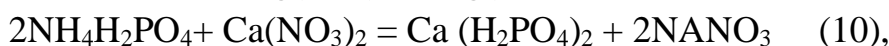
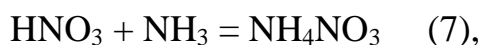
Impurities associated with apatite react with nitric acid:



Formed by reaction (1) HF reacts with silicic acid:



When a nitric acid solution of apatite is neutralized with gaseous ammonia, the following reactions occur:



As can be seen from the given reactions, the RFM, RAP additive consists of water-soluble (calcium and magnesium nitrates, ammonium, calcium, magnesium monophosphates, etc.) and water-insoluble (calcium and magnesium di- and triphosphates, sesquioxides, gels, silicic acid, hydrofluoric acid salts, etc.) compounds.

The results of the chemical analysis of the samples are given in Table 1, on the basis of which the following can be concluded:

1. The part of apatite SiO_2 insoluble in HNO_3 is found in sediments from the ACR storage facility, from the filter before the granulator and in the finished product. The presence of SiO_2 in the specified samples is explained by the incomplete separation of the insoluble residue in the settling tank during continuous operation.

Table 1

Results of chemical analysis of samples taken from various stages of ammonium nitrate RAP production

Samples	Contents, wt, %								Other components
	N		P ₂ O ₅			CaO			
	General	Ammonia.	General	Cit.	Water	General	Cit.	Water	
1	2	3	4	5	6	7	8	9	10
1. Apatite	-	-	39,6	-	-	50,4	-	-	R ₂ O ₃ -2,45 SiO ₂ -0,38 F-3,17
2. AQW from the sump	10,6	-	4,9	-	4,9	6,10	-	6,10	R ₂ O ₃
3. AQV from storage	11,0	-	4,42	-	4,42	5,82	-	5,82	R ₂ O ₃ -0,21
4. Neutralized AQV from ITN	21,0	10,2	4,23	2,08	1,52	6,40	5,91	2,89	R ₂ O ₃ -0,16
5. Neutralized AQV from DN	23,5	11,7	3,63	1,32	0,06	5,13	1,63	0,12	R ₂ O ₃ -0,05
6. Shelocaselites from storages	33.2	17,3	0,70	-	0,04	0,82	-	0,07	
7. Melt of saltpeter after evaporation. Apparatus of the second stage	33,9	18,0	0,79	0,38	0,05	0,95	0,82	0,15	
8. Melting saltpeter before granulation	33,9	17,0	0,84	0,41	0,06	1,13	0,74	0,22	
9. Finished product	34,5	17,8	0,88	0,52	0,05	0,96	0,73	0,10	R ₂ O ₃ -0,03
10. Sediment from the cell storage	22,6	11,2	9,99	0,53	0,14	17,7	0,95	0,11	MgO-0,11 R ₂ O ₃ -2,45
11. Filter cake before granulator	-	-	19,4	1,45	0,03	21,4	1,92	0,25	R ₂ O ₃ -2,85 SiO ₂ -1,15 Cationite - 37
12. Sediment from the granule zeroer	3,94	2,01	34,1	8,5	0,20	43,0	-	0,34	MgO-1,04 R ₂ O ₃ -1,28 SiO ₂ -0,05 Cationite - 20
13. Sediment from the AKV decanter	-	-	1,97	-	0,22	2,43	-	-	SiO ₂ -78
14. Sludge from the AKV storage facility	-	-	2,01	-	0,19	2,62	-	-	SiO ₂ -81
15. Sediment from the final evaporation apparatus	23,2	11,6	17,7	7,10	0,28	23,0	7,80	0,27	

Conclusion. The leakage of SiO₂ into the ammonium nitrate production system can be eliminated by switching the operation of the apatite decomposition reactor and the AKR settling tanks to a periodic mode. 2. Analysis of sediments from the liquor storage shows that they mainly consist of equal amounts of ammonium nitrate and tri-calcium phosphate. The accumulation of sediment in large quantities can be explained by the fact that during the storage

of liquors, calcium phosphates gradually settle to the bottom of the storage, forming a stationary mass with the ammonium nitrate solution, which cools over time and turns into a monolith as a result of the crystallization of ammonium nitrate. This phenomenon is also observed in pressure tanks for ammonium nitrate melt. The pouring of insoluble particles to the wall of the granulators occurs under the action of centrifugal forces, as a result of which the openings of the granulators narrow, which, in turn, leads to a deterioration in the granulometric composition of the product. For this reason, granulation towers are frequently (1-3 times a day) stopped to replace granulators.

3. In addition to ammonium nitrate, calcium phosphates and SiO_2 , cation exchanger is found in large quantities in the filter and granulator sediments. Its presence is explained by the unsatisfactory operation of the juice vapor condensate regeneration station, where the said cation exchanger is used. To prevent its penetration into the ammonium nitrate production process, it is necessary to completely capture it from the AC solutions returned to the system by installing special filters.

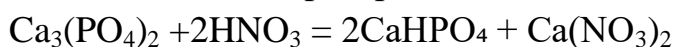
4. The adhesion of sediments to the inner surfaces of evaporators and communications occurs due to the relatively low speed of the solution movement near the walls of the tubular system and frequent load fluctuations. As a result, insoluble particles of the additive begin to settle on the inner surface of the tubular system, forming hard layered crusts. When the load decreases, the speed of movement of the melt through the pipes is sharply reduced, which leads to an increase in the adhesion process.

5. Analysis of the composition of the ACR apatite particles after the ITN apparatus shows that 85% of P_2O_5 is in citrate and water-soluble forms. After the alkalis are neutralized, the content of the citrate-soluble form of P_2O_5 decreases to 37%, and the water-soluble form to 1.65%. When it is mixed in storage with ammonium nitrate solution neutralized to an alkaline reaction, all P_2O_5 is converted into tricalcium phosphate.

Subsequently, during the evaporation of ammonium nitrate solutions in the apparatus of the second stage of evaporation and in the final evaporation apparatus, part of the P_2O_5 again passes into the citrate-soluble form. The content of the latter in the finished product reaches up to 70%. This is explained by the fact that during high-temperature evaporation of the ammonium nitrate solution, thermal decomposition of ammonium nitrate occurs according to the reaction:



The ammonia released in this process passes into the vapor phase, and nitric acid again interacts with tricalcium phosphate and converts it into dicalcium phosphate:



Thus, a significant portion of phosphorus in the RAP additive is in a form assimilable by plants, i.e., during the production of ammonium nitrate with the addition of RAP, additional phosphorus fertilizer is produced. From the above it follows that further improvement of the quality of ammonium nitrate by increasing the amount of RAP additive without improving the existing technology is not possible.

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