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SEPARATION OF Ca(II) AND Mg(II) IONS IN THE TECHNOLOGICAL SOLUTION FOR DOLOMITE PROCESSING

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ABSTRACT: Obtaining magnesium salt from unfired dolomite by nitric acid dissolution followed by neutralization with ammonia to pH 12 and separation of CaCO_3 by triple and quadruple dilution of the solution with water is not economically feasible. By nitric acid treatment of unfired dolomite, it is advisable to obtain an acidic solution containing $\text{Mg}(\text{NO}_3)_2 + \text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$ and use it as a strengthening additive in ammonium nitrate. If necessary, magnesium salts can be obtained from dolomite fired at 700-800 °C. When the suspension settles, $\text{Mg}(\text{OH})_2$ appears in the upper layer, which allows it to be roughly separated from other solid components by this method. To obtain relatively large crystals of $\text{Mg}(\text{OH})_2$ in suspension, quenching is carried out at 95-100 °C, heating the pulp containing ~ 17% of the solid phase with live steam. To separate $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, the pulp is diluted to a solid phase content of 11%, cooled to 60 °C and subjected to carbonization.

KEYWORDS: Dolomite, nitric acid, ammonia, neutralization, calcium and magnesium nitrate solution, conditioning additive.

I. INTRODUCTION

Ammonium nitrate (NH_4NO_3) is a universal nitrogen fertilizer containing 34.4% nitrogen. It is available in granular form, highly soluble in water. It is quickly absorbed by plants and can be used on all types of soil and for all crops. It is applied as the main fertilizer and as a top dressing, especially for winter grain crops, providing a yield increase of up to 5 centers' per 1 hectare. The result of its use: regulates the growth of vegetative mass; increases protein and gluten content in grain; increases crop productivity.

The volume of production of ammonium nitrate, a valuable fertilizer, is increasing.

A feature of ammonium nitrate and products based on it is thermal instability due to its oxidizing properties, which pose a threat of spontaneous decomposition with the release of heat during storage, in the absence of heat removal and ventilation, in the presence of organic substances [1]. Safety precautions during its storage, use, and production continue to be the focus of attention of specialists. Ammonium nitrate and fertilizers containing it are classified as "hazardous" by many national and international standards. According to the UN classification used in international transport regulations, ammonium nitrate is classified as Class 5.1. - oxidizing substances [2].

Thus, there is a patent [3] relating to the production technology of ammonium nitrate with a magnesium additive. The method involves introducing a magnesium additive obtained by decomposing magnesium-containing raw materials with nitric acid into the ammonium nitrate melt, neutralizing the resulting mixture, evaporation and granulation, while the magnesium additive is treated with a reagent containing phosphoric acid and/or its salts to a mass

ratio of P_2O_5/Fe in a solution of the magnesium additive 1.6-3.5, and a solution is used as a reagent after the separation of calcium from the nitrate extract of natural phosphates. The method makes it possible to increase the strength of ammonium nitrate granules by 10-18% and to use magnesium nitrate solutions with a high content of impurities, in particular iron, as a magnesium additive, while maintaining the quality of the finished product.

There is a known method [4] for producing non-caking ammonium nitrate, according to which a magnesium additive is introduced into its melt - a solution of magnesium nitrate obtained by decomposing caustic magnesite with nitric acid, treating the solution with an excess of caustic magnesite and separating the sediment, the mixture is neutralized with ammonia, evaporated, and granulated. The disadvantage of this method is the increased consumption of caustic magnesite and low filterability of the sediment due to the formation of finely dispersed iron hydroxide, which precipitates when the solution is treated with an excess of caustic magnesite.

There is a known method [5] for preparing a magnesium additive by decomposing caustic magnesite according to STATE STANDARD 1216 (Table 1).

Table 1. Content of caustic magnesite components

КОМПОНЕНТ	I class	II class	III class
MgO, not less than	87	83	75
Impurities, not more than			
CaO	1.8	2.5	4.5
$Al_2O_3 \cdot Fe_2O_3$	2	-	-
SiO_2	1.8	2.5	4.0
Loss on ignition	6	8	8
Moisture	1.5	1.5	1.5

The decomposition of caustic magnesite is carried out with 40-45% nitric acid in an amount of 105-110% of the stoichiometric one. Caustic magnesite of composition, %: MgO 84.16; CaO 4.17; R_2O_3 3.58; SiO_2 2.78 in an amount of 236 g with thorough mixing. As a result of the release of reaction heat, the reaction mass is heated to 1080C, the degree of magnesite dissolution is 96%. The insoluble precipitate is separated by filtration. A solution in an amount of 1070 ml has the composition: excess nitric acid, 10.9% MgO, 0.56% CaO and 0.5% R_2O_3 , the dried sediment in an amount of 160 g has the following composition: $Mg(NO_3)_2$ 64.9%, $Ca(NO_3)_2$ 4.74%, R_2O_3 8.15 in terms of nitrates.

The disadvantages of this method are that when magnesite interacts with 40-45% nitric acid, as a result of an increase in temperature to 108 °C or more due to the decomposition of nitric acid, a rapid release of nitrogen oxides is observed, while corrosion of equipment increases and the degree of use of magnesite does not exceed 97.5-98.0%.

Dolomite additive is used in a number of enterprises in the CIS and European countries. Dolomite contains 30-31% CaO and 19-20% MgO and is used as a conditioning additive that binds water in the ammonium nitrate melt, allowing one to obtain a practically anhydrous product. Its use reduces the caking of ammonium nitrate by increasing the strength of the granules. Dosing of calcium and magnesium nitrate solutions is carried out into ammonium nitrate solutions supplied for evaporation, based on the content of nitrate salts in the finished product being 0.2-0.5% (in terms of CaO).

The conditioning additive can be prepared either from dolomite or from a mixture of dolomite and magnesite. STATE STANDARD 2-85 for ammonium nitrate allows the use of calcium-containing additives, incl. and dolomite.

In this regard, the tasks of the chemical industry of Uzbekistan are: improving the physical and mechanical properties of nitrate by reducing the moisture content by evaporating nitrate solutions to a mass concentration of at least 99.7%, as well as introducing the magnesium additive $Mg(NO_3)_2$; improving its commercial properties by selecting a conditioning additive that reduces thermal instability and caking caused by hygroscopicity and modification transitions.

The main types of products of the chemical industry of the Republic of Uzbekistan are nitrogen fertilizers: ammonium nitrate and urea. Three large enterprises Navoiyazot JSC, Maksam-Chirchik JSC, Ferganaazot JSC annually produce more than 1.76 million tons of ammonium nitrate with a strengthening magnesium additive.

Ammonium nitrate is the most important nitrogen fertilizer produced both for domestic consumption and for export. The volume of its output is constantly growing. The main disadvantages of its commercial form are caking caused by hygroscopicity, solubility, modification transitions, and thermal instability [6].

One of the urgent tasks of its production is to improve its commercial properties: research is underway to select effective additives that improve the strength of granules and increase thermal stability [7]. The issue of caking is important for the transportation and storage of the product, and this, in turn, is associated with moisture absorption, hygroscopicity, and the presence of certain surfactants and other conditioning additives in the fertilizer.

Magnesium fertilizers (solid and liquid) have not previously been produced in the Republic due to the lack of modern technologies for processing local magnesium raw materials. The demand of chemical enterprises and the construction industry for magnesium compounds amounts to hundreds of thousands of tons. And to ensure imports, millions of foreign currency units are required.

Currently, to improve the physical properties of commercial ammonium nitrate, imported magnesite and brucite are used as a strengthening additive. In Uzbekistan, dolomites are a common magnesium raw material: the number of their deposits is up to 30, with a magnesium oxide content of more than 18%. They are located in Dekhkanabad, Saukbulak (Almalyk), Muruntau, Fergana (Mamai village), Navoi (Zametdin-1), Bukhara regions. The developed reserves of dolomite ore amount to more than 300 million tons.

In the production of ammonium nitrate, $\text{Mg}(\text{NO}_3)_2$ is used in the form of an aqueous solution, adding to the ammonium nitrate solution before evaporation. In industry, magnesium additive, used as a conditioning additive in granulated ammonium nitrate, is prepared in the form of a 26-32% solution of magnesium nitrate by decomposing magnesite powder with nitric acid according to the reaction.

A method has been developed for preparing a conditioning additive for ammonium nitrate, which makes it possible to reduce the consumption rate of magnesite by 2 times [8]. The process consists of the following stages: dissolution of dolomite in nitric acid in a reactor with a separation grid by forced circulation of the acidic solution; separation of the liquid phase from the solid phase by filtration; purification of dolomite nitrate solution from calcium ions by selective precipitation with ammonium sulfate at a temperature of 100-105 °C, precipitation duration (60-90) minutes, ammonium sulfate rate for 90% precipitation of calcium ion, filtration and separation of magnesium nitrate solution from calcium sulfate dihydrate-hemihydrate.

Purpose of the work: development of a method for producing a strengthening additive in ammonium nitrate by processing unfired dolomite to produce a mixture of $\text{Mg}(\text{NO}_3)_2 + \text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$ and subsequent selective extraction of Ca^{2+} ions from this dolomite extract.

Methods and materials. The object of study is dolomite from the Dekhkanabad deposit. Standard laboratory chemical-analytical methods for studying raw materials, laboratory technological, enlarged pilot-industrial approaches to methods of its processing were used, with the subsequent development of technology for obtaining the required derivatives from dolomite, as well as its implementation at JSC "Maksam-Chirchik".

Results and discussions. The method for separating Ca^{2+} and Mg^{2+} ions included two the following stages.

1) dissolving dolomite in nitric acid, obtaining a dolomite extract - solution ($\text{Mg}(\text{NO}_3)_2 + \text{Ca}(\text{NO}_3)_2$). Dolomite from the Navbakhor deposit had the composition: CCa 20.62%; CMg 13.136%. A 210 g sample of dolomite was dissolved in 800 cm³ of nitric acid (30 % mass), at room temperature, time 2 hours. The solution was filtered, separated from insoluble substances and analyzed (Table 2).

Table 2. Results of analysis of dolomite extract

Dolomite	HNO_3 , 30%	Filtrate			
Mass, g	V, dm ³	V, dm ³	ρ , g/cm ³	Mg, g/cm ³	Ca, g/cm ³
210.0	0.8	0.76	1.315	31.1	57.4

Table 3. Result of 4-fold dilution during carbonization, ref. solution (g), V 0.1 dm³

Name	Experiment 1	Experiment 2	Experiment 3
	Vf. 0.60 dm ³ Sediment mass 21 g	Vf. 0.68 dm ³ Sediment mass 16,3 g	Vf. 0.68 dm ³ Sediment mass 16.5 g
Stock solution, (g)			
Ca	5.7	5.7	5.7
Mg	3.1	3.1	3.1
Filtrate, (g)			
Ca	0.4	0.3	0.5
Mg	3.3	2.4	2.8
Sediment, (g)			
Ca	4.8	4.9	5.5
Mg	0.5	0.8	0.5

Table 4. Result of 3-fold dilution during carbonization, ref. solution (g), V 0.1 dm³

Name	Experiment 1	Experiment 2	Experiment 3
	Vf. 0.60 dm ³ Sediment mass 18.3 g	Vf. 0.68 dm ³ Sediment mass 16 g	Vf. 0.68 dm ³ Sediment mass 16.5 g
Stock solution, (g)			
Ca	5.7	5.7	5.7
Mg	3.1	3.1	3.1
Filtrate, (g)			
Ca	0.3	0.5	0.5
Mg	2.8	2.1	2.3
Sediment, (g)			
Ca	5.5	4.8	5.4
Mg	0.6	1.3	1.2

2) Selection of a method for separating Ca²⁺ and Mg²⁺ ions in a dolomite extract solution. The method is based on the precipitation of Ca²⁺ ions from a mixed solution of Ca(NO₃)₂ and Mg(NO₃)₂ by converting Ca²⁺ and Mg²⁺ ions into hydroxide forms by treating the extract with 25% ammonia water to pH 12 at temperature 60 °C. The resulting solution was diluted with water. Carbonation was carried out with carbon dioxide to pH 7.0: calcium was precipitated in the form of CaCO₃, and Mg²⁺ remained in solution. When diluting the original solution, 3 options were tested: dilution by 4 times (Table 3); dilution by 3 times (Table 4); dilution by 2 times (Table 5).

Table 5. Result of 2-fold dilution during carbonization, ref. solution (g), V 0.1 dm³

Name	Experiment 1	Experiment 2	Experiment 3
	Vf. 0.37 dm ³ Sediment mass 17.5 g	Vf. 0.38 dm ³ Sediment mass 17 g	Vf. 0.41 dm ³ Sediment mass 15.5 g
Stock solution, (g)			
Ca	5.7	5.7	5.7
Mg	3.1	3.1	3.1
Filtrate, (g)			
Ca	0.3	0.3	0.5
Mg	2.1	2.0	2.0
Sedi-ment, (g)			
Ca	5.6	5.6	5.03
Mg	1.3	1.4	1.03

Analysis of the data at Table 3 shows that the content of Ca²⁺ ions in the sediment is 89%, Mg ions in the filtrate - 91% of the original amount. From Table 4 it follows: Ca²⁺ ions in the sediment are 92%, Mg²⁺ ions in the filtrate are 77% of the original. From Table 5 it follows: Ca²⁺ ions in the sediment - 95%, Mg²⁺ ions in the filtrate - 66% of the original. As a result, the main part of Ca²⁺ passes into the sediment, and Mg²⁺ remains in the filtrate; the degree of transition of Mg²⁺ into the sediment depends on the dilution factor. With a dilution factor of 4.9%, Mg²⁺ passes into sediment, and with a dilution factor of 3-23%.

Thus, a solution of magnesium hydroxide can be obtained from dolomite using the following technology: - dissolving dolomite in 30% nitric acid; - treatment of a solution of nitric acid extract of dolomite with a 25% ammonia solution to pH 12; - 3x and 4x dilution of the solution with water; - precipitation of CaCO₃ by passing CO₂ to pH 7; - removal of CaCO₃ by filtration or settling of the solution; - from a solution of Mg(OH)₂ and NH₄NO₃ with Ca(OH)₂ impurities, depending on the concentration of NH₄NO₃, crystals of Mg(NO₃)₂·6H₂O or Mg are obtained (NO₃)₂·6H₂O+NH₄NO₃, or, with a NH₄NO₃ concentration above 32%, NH₄NO₃ crystals with Mg(NO₃)₂ in solution.

To separate a mixture of Mg(OH)₂ and NH₄NO₃, it is necessary to evaporate the solution and crystallize NH₄NO₃. NH₄NO₃ crystals will partially entrain Mg(OH)₂, and its absolute amount in the solution will decrease.

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