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STUDY OF THE PROCESS OF DECOMPOSITION OF DOLOMITE "SHORSU" WITH NITRIC ACID TO OBTAIN A SOLUTION OF CALCIUM AND MAGNESIUM NITRATES

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Abstract . This article examines the possibility of obtaining a solution of calcium and magnesium nitrates by decomposing dolomite m.r. "Shorsu" with nitric acid. The process of decomposition of dolomite with nitric acid was studied depending on the concentration of the acid and temperature.
Key words: dolomite, nitric acid , solution of calcium and magnesium nitrates.

Currently, throughout the world, with intensive population growth, reduction of suitable land resources and water reserves, the role of production of new types of fertilizers is increasing to fully satisfy the population's need for high-quality products.

One of the effective ways of producing mineral fertilizers is to obtain them in liquid form. The production of such fertilizers leads to a reduction in a number of processes and, compared to solid fertilizers, to a noticeable reduction in costs.

Today, one of the important tasks is the development and improvement of technologies for obtaining new complex-action fertilizers based on local raw materials.

To solve this problem, it is important to use as a raw material the products of nitric acid decomposition of dolomite (a solution of calcium and magnesium nitrates) followed by enrichment with components of nitrogen fertilizers, physiologically active substances and microelements.

In order to provide a physicochemical justification for the process of obtaining a liquid fertilizer with a complex effect, containing in its composition simultaneously nitrogen, calcium, magnesium, potassium, copper and a physiologically active substance, studies were conducted to study the process of decomposition of dolomite with nitric acid to obtain a solution of calcium and magnesium nitrates, followed by enrichment with fertilizer components and microelement-containing compounds.

In order to obtain calcium and magnesium nitrates based on dolomite from the Shhorsu deposit, the process of its decomposition with nitric acid was studied depending on the acid concentration (30÷57%), temperature (30÷50°C), process duration and acid feed rate [1,2].

According to chemical analysis, dolomite from the Shorsu mine has the following chemical composition (Table 1.)

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Table-1.
Chemical composition of dolomite sample (wt.%)

Name dolomite deposits	Content in % on air dry matter												
	CaO	MgO	Al2O3	Fe2O3 + FeO	FeO	SiO2	MnO	TiO2	Na2O	K2O	P2O5	SO_3 O total	CO2
m.r. "Shorsu"	31.48	19.17	0.32	0.29	0.25	2.87	0.01	0.02	0.05	0.15	0.03	0.3	45.0

X-ray phase and thermal methods of analysis of dolomite from the Shorsu mine confirmed the results of chemical analyses of the high content of calcium and magnesium carbonates in the cheese [3].

The process of decomposition of dolomite with nitric acid, as well as with hydrochloric acid, is accompanied by strong foaming, therefore this process should be carried out in two stages. That is, at the first stage with 35÷40% of the nitric acid rate, and at the second stage of the process with the remaining 60÷65% of the acid rate.

The concentration of nitric acid used was 30, 40 and 57%. The process temperature was 30, 40 and 50°C.

Based on the results of studying the process of decomposition of dolomite with nitric acid, it was found that the optimal concentration of the acid is 40%, at which a solution is formed containing 41÷42% of the sum of calcium and magnesium nitrates. When decomposing dolomite with 30% nitric acid forms a solution with a concentration of 29-30% of the sum of calcium and magnesium nitrates. In the case of using 57% nitric acid a saturated nitric acid pulp is formed and crystallization of calcium and magnesium nitrates occurs. This phenomenon is undesirable, since it complicates the process of separating the insoluble residue from the crystals of calcium and magnesium nitrates.

Therefore, foaming during nitric acid decomposition of dolomite of the Shorsu mine in two stages was studied depending on the time and rate of supply of acid with a concentration of 40.0%, at a temperature of 30÷40 ^{0}C.

From the data given in table 2 it follows that during the decomposition of the "Shors" dolomite with 40% nitric acid at a feed rate of V=7.0 g/min at the first stage of decomposition, i.e. with a 40% acid rate, the maximum foam multiplicity value is Kn=4.50. At the second stage (with the final decomposition of the dolomite with the remaining 60% acid rate), the multiplicity value was Kn=7.13.

The results of the research are presented in Table 2.

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Table-2
Change in foam multiplicity depending on time and feed rate of nitric acid during 2-stage decomposition of dolomite

Norm 31% nitric acid, %	Duration of time, min.														
	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30
acid feed rate V = 7.0 g/min															
1st stage 40.0	2.25	3.13	4.50	1.18	4.38	1.0	0.88	0.75	0.63	0.50	0.38	0.25	0.12	0	0
II stage 6 0, 0	3.25	4.00	4.88	5.50	6.25	7.13	6.13	4.0	2.38	1.25	0.88	0.75	0.50	0.37	0.13
acid feed rate V= 5.0 g/min															
I stage 40.0	0	0.91	1.68	3.51	2.32	1.36	1.24	0.92	0.94	0.89	0.75	0.63	0.48	0.36	0.25
II stage 60.0	2.6	2.84	3.45	4.30	4.85	5.6	5.75	4.82	3.34	2.35	1.46	1.24	0.96	0.73	0.46
acid feed rate V= 2.5 g/min															
1st stage 40.0	0	0.75	1.0	1.38	1.75	2.0	1.38	1.25	1.13	1.0	0.88	0.75	0.62	0.38	0.25
II stage 60.0	1.26	1.38	1.38	1.40	1.62	1.74	1.74	1.86	1.99	1.99	1.48	1.36	1.24	0.98	0.75

In the process of dolomite decomposition with nitric acid supplied at a rate of V=5.0 g/min., at the first stage the maximum foam multiplicity was Kn=3.51, and at the second stage Kn=5.75. When acid was supplied at a rate of V=2.5 g/min., the maximum foam multiplicity at the 1st stage was Kn=1.56, and at the 2nd stage Kn=1.99.

In this way, it is possible to achieve a reduction in the foam multiplicity value, i.e. to eliminate abundant foaming in the process of two-stage nitric acid decomposition of the Shorsu dolomite.

Based on the obtained results, the optimal technological parameters of the process of nitric acid decomposition of dolomite were established : concentration HNO_3 -40.0% temperature 30÷40 ^{0}C and acid feed rate 2.5÷5.0 g/min, and decomposition should be carried out in two stages.

The obtained results served as the basis for recommending a basic process flow diagram for obtaining a solution of calcium and magnesium nitrates, which consists of the following stages:

Two-stage decomposition of dolomite "Shorsu" with nitric acid is carried out:

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- two-stage decomposition of dolomite with nitric acid;
- purification of the resulting suspension from insoluble residue;
- purification of exhaust gases (separation of CO2 and dolomite dust from equipment);

Figure 1 shows the process flow diagram for obtaining a solution of calcium and magnesium nitrates.

According to the scheme, dolomite from the warehouse enters the bunker (1), then is fed to the belt weigh batcher (2) and from there to the screw mixer (3). At the same time, 40% nitric acid in the amount of (35-40% of the total consumption rate) is fed to the screw mixer from the storage tank (4) through the diaphragm batcher (7) to carry out partial decarbonization.

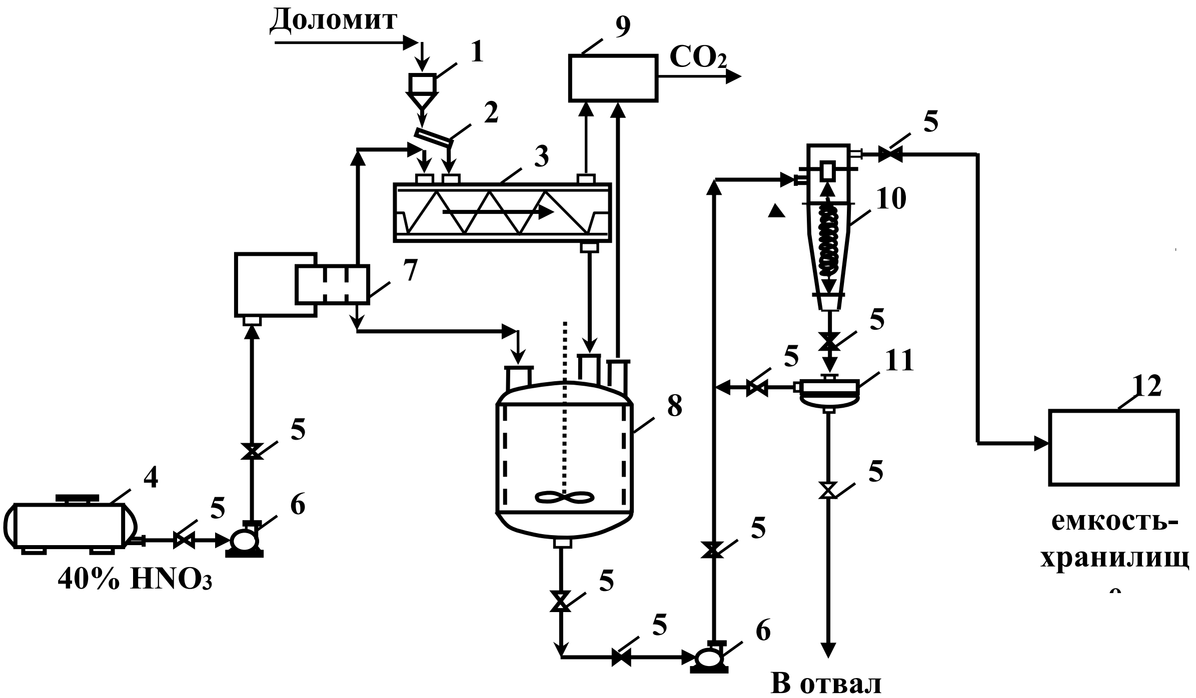

Fig . 1. Basic technological scheme for obtaining a solution of calcium and magnesium nitrates

1-hopper; 2-belt weigher; 3-screw mixer; 4-storage tank; 5-valves; 6-centrifugal pumps; 7-diaphragm acid dispenser; 8-dolomite decomposition reactor; 9-cyclone; 10-hydrocyclone; 11-settler; 12-storage tank for calcium and magnesium nitrate solution.

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In the screw mixer, dolomite is partially decomposed by nitric acid to form a pulp, which is fed into the reactor (8). In the reactor (8), the remaining part of the dolomite is decomposed (60-65% rate)
nitric acid. From the reactor (8), the pulp obtained is fed by a centrifugal pump (6) to a hydrocyclone (10), where the insoluble residue is separated from the solution of calcium and magnesium nitrates. The clarified solution of calcium and magnesium nitrates is fed to a storage tank (12) and is used to obtain a liquid fertilizer of complex action.

Insoluble thickened residues from the hydrocyclone enter the settling tank (11) through the pipes. Where after a certain time the suspension settles to the bottom of the equipment. The purified solution is returned to the process, and the sediment is removed from the bottom and goes to the dump.

The gas-dust mixture (nitric acid, dolomite dust, drops of calcium and magnesium nitrates) released from the screw mixer (3) and the reactor (8) is fed into the upper part of the cyclone (9). In the cyclone , the acid droplets and CO2 are separated . The carbon dioxide is released into the atmosphere, and the acid droplets are collected and returned to the process.

A pilot batch of calcium and magnesium nitrate solution was obtained on a large laboratory setup. The obtained product contains 41÷42.0% of the sum of calcium and magnesium nitrates and has the following physicochemical properties: crystallization temperature -11.0°C, density 1.3961 g/cm³, viscosity 3.013 mm²/s and pH of the medium 1.15. This solution can be used to obtain a complex liquid fertilizer containing both calcium nitrate and magnesium nitrate.

Conclusion. Thus, the optimal technological parameters of the process of nitric acid decomposition of dolomite have been established: HNO3 concentration - 40.0 %, temperature 30÷40 ^{0} C and acid feed rate 2.5÷5.0 g/min, and decomposition should be carried out in two stages.

A basic process flow diagram for obtaining a solution of calcium and magnesium nitrates has been developed.

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