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*A.S. Savenkov, I.S. Bilohur***PROCESSING OF LOW-GRADE ROCK PHOSPHATE INTO COMPLEX FERTILIZERS****National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine**

There is a great quantity of low-grade phosphorite deposits in Ukraine, in which  $P_2O_5$  content is about 5–10 wt.%. In this work we developed the process of the manufacture of fertilizer from phosphorites with low content of phosphorus (V) oxide using nitric acid. The results of thermodynamic calculations and X-ray phase analysis revealed a multiple-choice composition of acid baths; the equilibrium composition of components was determined too. It was shown that the formation of phosphoric acid and macronutrient element (K, Ca, Mg, and Fe) occurs when the ratio of liquid phase to solid phase is 1.25–1.75  $cm^3/g$  and the temperature is 47–97°C. A pilot installation was created and the method of experimental study in a wide interval of parameter changes was proposed. Experimental results showed the effects of technological parameters on the  $P_2O_5$  extraction ratio into solution which reaches 98–99 wt.%. The following conditions are recommended for the low-quality phosphorous-containing raw material: temperature of 40–60°C,  $HNO_3$  content of 54–58 vol.%,  $HNO_3$  rate of 110–120%, the duration of decomposition of 30–40 min, and the intensity of mixing  $Re$  of 100–900. The results of theoretical and experimental studies allowed suggesting manufacturing scheme of production of complex NPCa-fertilizer involving the following steps: decomposition of low-quality phosphorous-containing raw material by nitric acid; filtration of nitrogenous acid bath with the release of insoluble components ( $SiO_2$ ); neutralization of clarified nitro-acid solution with the isolation of  $CaHPO_4$ ; final neutralization; evaporation; mixing with  $CaHPO_4$ ; dehumidification; grinding, dissemination and packaging of prepared product. The main physicochemical properties of the developed fertilizer were determined. The obtained fertilizer contains (in wt.%): 46–50  $NH_4NO_3$ , 30–35  $Ca(NO_3)_2$ , 10–12  $CaHPO_4$ , 3.8–4.1  $FePO_4 \cdot 2H_2O$ , 2.6–3.9  $AlPO_4$ , 0.8–1.0  $KNO_3$ , 1.1–1.5  $Mg(NO_3)_2$ , and 0.05–0.10  $NaNO_3$ .

**Keywords:** low-grade phosphorites, mineralogical composition, nitric acid, decomposition, thermodynamics, technology.

**Introduction**

An actual problem of the chemical industry connected with mineral fertilizers output is the creation of a raw materials base, especially, for the products containing phosphorus, and the development of high efficient, economically valuable and environmentally clean technologies of complex processing of phosphorus containing raw materials with low  $P_2O_5$  content.

Special place of the phosphorus fertilizers among others could be explained by the fact that phosphorous and its compounds play important role in plants' and animals' life; they also reinforce the effectiveness of copper and nitrogen fertilizers action in soil.

We performed the studies on processing of the lean phosphate ores (with  $P_2O_5$  concentration of 5–

10%). That requires the follows: (a) theoretical and practical knowledge of the physicochemical properties of the raw material; (b) conduction of the thermodynamic studies for the determination of possible reactions' pathways at each stage of the fertilizers production; and (c) determination of kinetic and technological parameters of the process [1–8].

The acid processes are typically used for the processing of the low-quality phosphate ore, including nitric and hydrochloric acids, allowing performing in a relatively easy way the selective separation of formed solid content and solution already at the stage of the ore acid treatment, which is a sort of chemical enrichment of poor phosphate ore.

**Experimental design. Thermodynamic study**

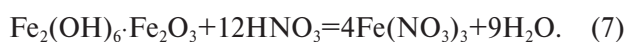
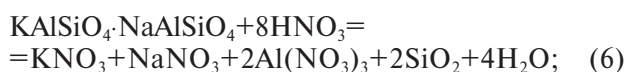
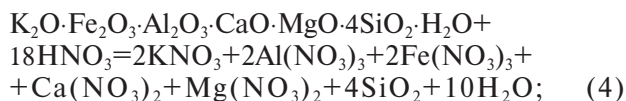
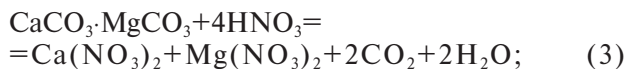
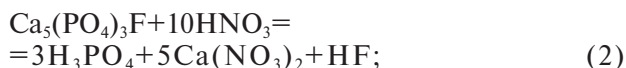
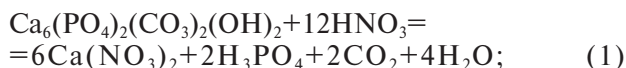
We carried out nitric-acid decomposition of low-grade phosphorites of Kharkiv-Donetsk geological region. The mineralogical composition of

the given materials was as follows (wt.%): 3–5 carbonate-hydroxylapatite [ $\text{Ca}_6(\text{PO}_4)_2(\text{CO}_3)_2(\text{OH})_2$ ]; 27–29 fluorapatite [ $\text{Ca}_5(\text{PO}_4)_3\text{F}$ ]; 21–23 calcium carbonate [ $\text{CaCO}_3$ ]; 0.5–0.9 magnesite [ $\text{MgCO}_3$ ]; 13.0–15.0 glauconite [ $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot\text{MgO}\cdot\text{CaO}\cdot\text{Fe}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 6\text{H}_2\text{O}$ ]; 0.8–1.0 feldspars [ $\text{K}_2\text{O}\cdot\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 6\text{SiO}_2$ ]; 1.9–2.1 nepheline [ $\text{NaAlSiO}_4\cdot\text{KAlSiO}_4$ ]; 0.4–0.6 limonite [ $\text{Fe}_2(\text{OH})_6\cdot\text{Fe}_2\text{O}_3$ ]; and 26–28 quartz [ $\text{SiO}_2$ ]. The chemical composition was as follows (wt.%): 29.0–37.2  $\text{SiO}_2$ ; 3.39–6.36  $\text{Al}_2\text{O}_3$ ; 3.36–8.08  $\text{Fe}_2\text{O}_3$ ; 0.20–0.38  $\text{TiO}_2$ ; 22.1–32.5  $\text{CaO}$ ; 0.47–1.30  $\text{MgO}$ ; 6.8–8.4  $\text{P}_2\text{O}_5$ ; 0.06–0.13  $\text{Na}_2\text{O}$ ; 0.51–1.93  $\text{K}_2\text{O}$ ; and 0.76–0.91 F.

The usage of nitric acid belongs to the most modern and promising trends of technological processes because nitric solutions are not only the source of nitrogen, but also increase the accessibility to the final suspension phosphatic part. This fact is the main agrochemical advantage of nitric-acid conversion of phosphates compared to other methods.

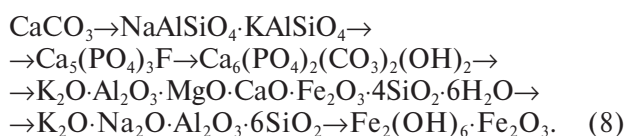
To determine possible reactions of nitric acid interacting with mineralogical composition, the thermodynamic researches were carried out. Taking into account the chemical composition of the material, we established the reaction paths, which take place when the material interacts with nitric acid. Thus, both physicochemical properties of the components and general patterns of compatibility with nitric acid were considered.

Standard thermodynamic characteristics of feed material components and the products of their interaction with  $\text{HNO}_3$  were taken from reference literature. For the materials, which do not have literature data on standard values of  $\Delta H_{298}^0$ ,  $\Delta S_{298}^0$ ,  $C_{p298}^0$  (i.e. heat content, entropy and heat capacity, respectively), we found them by means of methods given in literature [9–12]. The analysis of thermodynamic researches is grounded on consideration of the following reaction paths:



The results of thermodynamic analysis permit determining the equilibrium degree of decomposition of each mineral constituent; feed materials interacting with nitric acid are also given in Table. The choice of the temperature (323 K) is validated by the analysis of numerous literature data on phosphate and apatite decomposition.

In Table, L:S (in  $\text{cm}^3/\text{g}$ ) denominates the ratio between the content of each component in liquid and solid phases. The following transformation chain can be written:



Similar analyses were performed for the

Parameters of the raw materials (temperature 323 K;  $\text{HNO}_3$  content 56 wt.%)

L:S, $\text{cm}^3/\text{g}$	Raw material components' decomposition level (unit fractions)						
	carbonated hydroxyl-apatite	fluorapatite	calcite	glauconite	feldspars	nepheline	limonite
0.50	0.350	0.400	0.920	0.300	0	0.830	0
0.75	0.570	0.600	0.950	0.500	0	0.890	0
1.00	0.700	0.740	0.970	0.630	0	0.930	0
1.25	0.810	0.820	0.980	0.730	0.13	0.960	0.10
1.50	0.860	0.880	0.990	0.810	0.34	0.980	0.28
1.75	0.934	0.939	0.995	0.888	0.55	0.990	0.46
2.00	0.982	0.981	0.996	0.939	0.74	0.996	0.62
2.25	0.994	0.996	0.998	0.972	0.88	0.997	0.79
2.50	0.995	0.996	0.998	0.980	0.98	0.997	0.93

temperature range of 318 K to 373 K. In order to develop the procedure of the production of complex fertilizations on the basis of low-grade stock, physicochemical and kinetic investigations of the interaction processes should be carried out in a wider range of technological parameters.

#### **Experimental study**

The rate of phosphate decomposition by nitric acid, analogous to any other heterogeneous process, depend on the following factors: quantitative and qualitative phosphate composition, degree of fineness of the raw material, the strength and the fraction of acid, the temperature of the process, the decomposition duration and the rate of reagent interfusion.

For the implementation of the study of nitric-acid decomposition, the experimental arrangements were set up (Fig. 1). The milling of the feed material was performed in the globe mill (BM) and the classifier (C). A fine fraction of 0.25 mm size goes through an intake tank (IT<sub>2</sub>) and then through a capacitometer (CM<sub>2</sub>) is directed to the reactor (RA). The nitric acid is supplied by a capacitometer (CM<sub>1</sub>) to the reactor (R) which is made of glass. Further it moves to the thermostat and lidded.

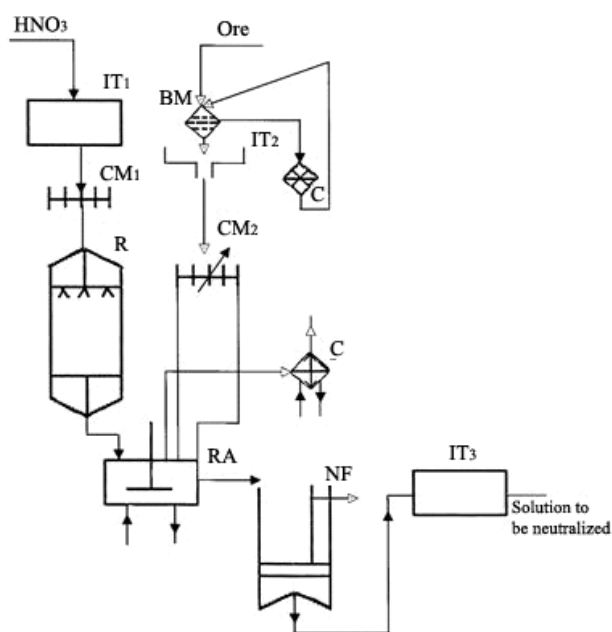


Fig. 1. Scheme of the experimental installation for interaction of nitric acid with phosphorus-containing raw materials

For the interfusion of the reacting mass, two-bladed stirrer (TBS) is taken with the regulated speed.

In the cage cover, a mercury thermometer for measuring the temperature of the reacting mass and an air sampling tube with a surface thermometer were used.

The resulting nitric acid solution (NAS) was supplied to the vacuum filter (NF) and the obtained clarified solution was directed to the collector (IT<sub>3</sub>) and then to the neutralization. Abductions of the gaseous reaction products were provided through the vent, where the gas comes to the condenser (C) with forced cooling and sent for analysis.

The samples of the solution, the sludge and the gas were collected and analyzed for required components (P<sub>2</sub>O<sub>5</sub>, N<sub>2</sub>, CaO, K<sub>2</sub>O, F, MgO, CO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>) by the methods of atomic absorption spectroscopy, X-ray diffraction analysis, potentiometry, colorimetry and gravimetry. The phosphorite – nitric acid – water system was investigated changing the values of technological parameters as stated below:

- HNO<sub>3</sub> concentration (wt.%): 25, 35, 45, 55, and 65;
- HNO<sub>3</sub> fraction (%): 90, 100, 103, 105, 107, 110, 113, and 115;
- temperature (°C): 25, 35, 40, 45, 50, and 60;
- interaction time (min): 5, 10, 15, 30, and 45;
- stirring intensity (expressed in Reynolds number): 200, 400, 600, 800, and 1000.

The HNO<sub>3</sub> fraction here and below implies the following. Industrial decomposition of phosphate raw materials, due to high calcium content and admixtures in the crude, is usually carried out at elevated nitric acid consumption. At the fraction of nitric acid equal to 100% of stoichiometric value for the decomposition of phosphate raw materials, the reaction under the normal conditions passes exhaustingly and its rate is high. The reduction of the acid fractions to, for example, 40%, results in the appearance of water-insoluble phosphates which requires special conditions.

Figs. 2–5 show the effect of results of the changes of the technological parameters on the P<sub>2</sub>O<sub>5</sub> extraction ratio.

#### **Results and Discussion**

It follows from the results of our investigation that the 98–99% efficiency of P<sub>2</sub>O<sub>5</sub> extraction is reached at temperatures of 40–60°C (Fig. 2). A further increase in temperature (over 60°C) seems to be impractical because of the increased nitric acid waste due to nitric oxide release into the vapor-phase and the enrichment of atmosphere corrosiveness. At lower temperature (less than 25°C), the rate of the process decreases due to the film formation of the calcium nitrate.

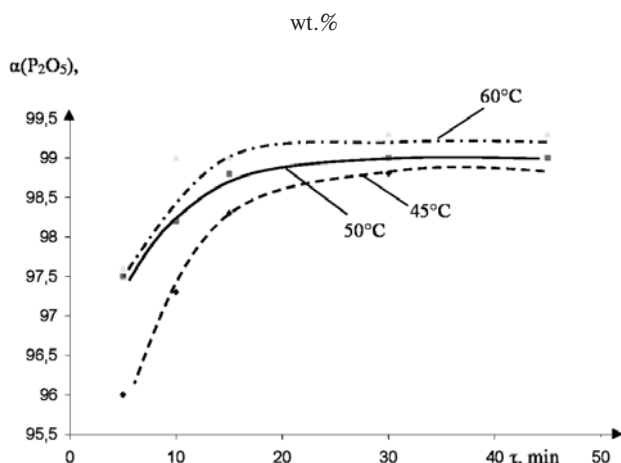


Fig. 2. Dependence of effectiveness of  $P_2O_5$  extraction (in wt.%) on the process duration at different temperatures ( $C_{HNO_3}=56$  wt.%;  $H_{HNO_3}=112\%$ ;  $L:S=1.7$  cm<sup>3</sup>/g)

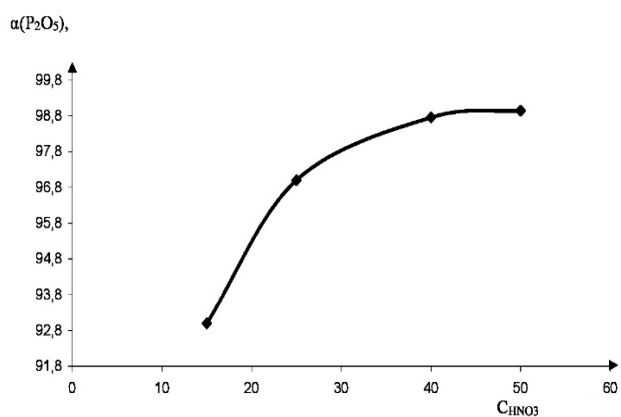


Fig. 3. Dependence of effectiveness of  $P_2O_5$  extraction (in wt.%) on  $HNO_3$  concentration (in wt.%) ( $T=60^\circ C$ ;  $t=30$  min;  $H_{HNO_3}=112\%$ ;  $L:S=1.7-1.8$  cm<sup>3</sup>/g)

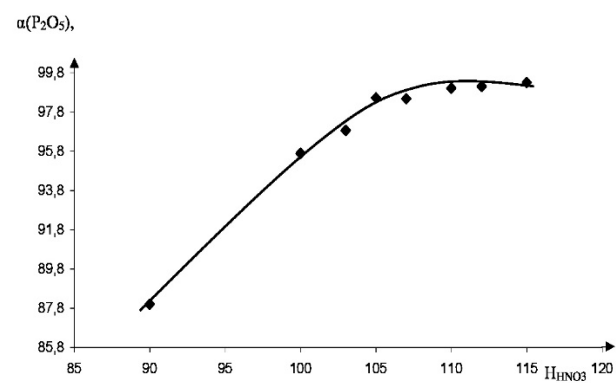


Fig. 4. Dependence of  $P_2O_5$  extraction effectiveness (in wt.%) on raw material nitric acid fraction (H) ( $T=60^\circ C$ ;  $t=30$  min;  $C_{HNO_3}=56$  wt.%;  $L:S=1.7$  cm<sup>3</sup>/g)

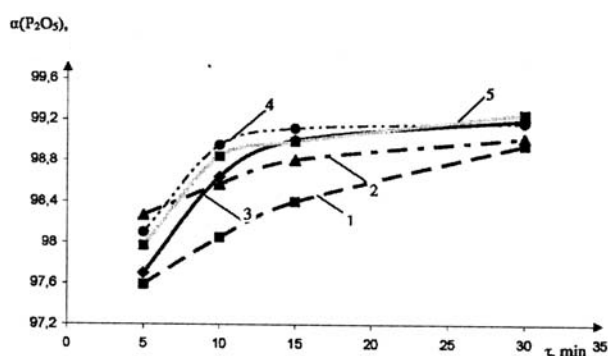


Fig. 5. Influence of temperature and stirring intensity on  $P_2O_5$  extraction effectiveness: 1 –  $T=45^\circ C$ ,  $Re=580$ ; 2 –  $T=50^\circ C$ ,  $Re=580$ ; 3 –  $T=60^\circ C$ ,  $Re=280$ ; 4 –  $T=60^\circ C$ ,  $Re=580$ ; 5 –  $T=60^\circ C$ ,  $Re=900$

The concentration of nitric acid during the interaction was 47–58 vol.%  $HNO_3$  (Fig. 3), it has little effect on the extraction effectiveness of  $P_2O_5$  from phosphorites. The results of the experiments demonstrated that the excess of acid regarding to its stoichiometric amount of 10–20% provides complete extraction of  $P_2O_5$  from the feedstock (Fig. 4).

Our findings also showed that the decomposition of the raw material proceeds at high rate and full interaction is achieved within 10–30 min. If the stirring intensity is  $Re=280$  (Fig. 5), the maximum  $P_2O_5$  extraction ratio of 98–99 wt.% is achieved.

Thus, the following technological parameters should be recommended for the decomposition of a phosphorus-containing low-grade raw materials: temperature of 40–60°C,  $HNO_3$  concentration of 54–58 vol.%,  $HNO_3$  rate of 110–120%, the decomposition duration of 30–40 min, and the stock stirring intensity of  $Re=100-900$  [13,14].

The results of the theoretical and experimental studies allowed offering a technological scheme of complex NPCa-fertilizer production, including the following stages: decomposition of phosphorus-containing low-grade raw materials with nitric acid; filtration of nitric-acid solution with extraction of insoluble substances (e.g.  $SiO_2$ ); neutralization of the defecated nitric-acid solution by extraction of  $CaHPO_4$ ; additional neutralization; evaporation; mixing with  $CaHPO_4$ ; drying; milling; sieving and packaging of the finished product. The key diagram of complex NPCa-fertilizer production is demonstrated in Fig. 6.

Phosphorous-containing raw material from the bunker (B) is directed to the reactor (RC1) by a screw feeder together with nitric acid (54–56 vol.%).



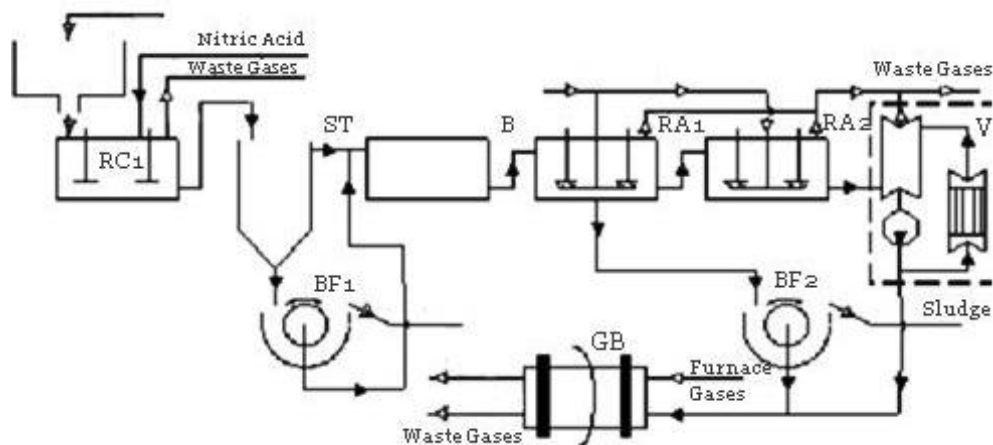


Fig. 6. Scheme of process flow for obtaining of N:P:Ca-fertilizers

The decomposition occurs at 50–60°C with the formation of nitric acid solution (NAS), that is later directed to the filter (BF1) where insoluble components are separated.

The insoluble sludge mainly consisting of SiO<sub>2</sub> (96–98 wt. %) undergoes drying and is directed for reprocessing into different wares [15]. The NAS is subjected to maturation in the settling tank (ST) before filtration. After filtration the clarified nitric acid solution is directed to the collector (B) and neutralized in reactor (RA1).

Neutralization of the clarified solution is conducted with ammonia and after achieving pH 2.9–3.1 a generated suspension is directed to the filter (BF2) for extraction of the solid phase in the form of CaHPO<sub>4</sub>. After filtration the solution is additionally neutralized (pH 6–7). After neutralization the pulp is directed to the vaporizer (V) where the main amount of water is eliminated at 130–140°C. The vaporized concentrated solution is further mixed with CaHPO<sub>4</sub>, carried to the granulation in (BG) and transferred to the finished product storage.

### Conclusions

We performed complex of physicochemical studies and established the foundations to develop the procedure of the production of nitrogen phosphorus fertilizers.

The mineralogical composition of the Kharkiv-Donetsk Geological region is detected. It includes fluorapatite, carbonated hydroxyl-apatite, glauconite, calcite, feldspars, quartzite and limonite.

The theoretical and thermodynamic analysis of the interaction during the nitric acid decomposition of phosphorites is conducted. The composition of acidic solutions, equilibrium composition of the reagents and process parameters

of interaction were evaluated as follows: HNO<sub>3</sub> concentration (vol.%) of 54–58, the excess is 6–12% of the stoichiometry value, process temperature of 40–60°C, decomposition duration of 30–40 min, stirring intensity (in the Reynolds number) in the range between 100 and 900.

The technological scheme of the production of complex fertilizer based on the low-grade phosphorites was proposed, the final product contains (wt.%): 46–50 NH<sub>4</sub>NO<sub>3</sub>; 30–35 Ca(NO<sub>3</sub>)<sub>2</sub>; 10–12 CaHPO<sub>4</sub>; 3.8–4.1 FePO<sub>4</sub>·2H<sub>2</sub>O; 2.6–3.9 AlPO<sub>4</sub>; 0.8–1.0 KNO<sub>3</sub>; 1.1–1.5 Mg(NO<sub>3</sub>)<sub>2</sub>; 0.05–0.1 NaNO<sub>3</sub>; pH 6–8.

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