УДК 661.833

O. B. Dormeshkin, D. Sc. (Engineering), assistant professor, vice-rector for research (BSTU);
A. N. Gavrilyuk, assistant lecturer (BSTU);
G. H. Cherches, PhD (Engineering), senior researcher (BSTU)

INFLUENCE OF CERTAIN TYPES OF PHOSPHATE RAW MATERIALS ON THE TECHNOLOGICAL PROCESS OF PRODUCTION EXTRACTION PHOSPHORIC ACID AND COMPLEX FERTILIZERS

Research on definition of phase structure of various sources of phosphate raw materials was carried out. The possible material compositions of the studied natural phosphate are calculated on the basis of cations and anions balance according to their charge. Comparative analyses of technological parameters of the production of phosphoric acid during the transition to alternative forms of phosphate raw materials is executed.

Introduction. The production of complex fertilizers is the most progressive branch of basic chemistry. The variety of options to combine the elements in their composition (N, P, K) determines the diversity of these fertilizers. It is the use of complex fertilizers that will allow us to reduce costs for fertilization by 65–70% and optimize a mineral nutrition of plants, which is practically very difficult when using simple forms of fertilizers.

The only manufacturer of complex fertilizers in Belarus is JSC "Gomel Chemical Plant." The problem of phosphate fertilizer production in Belarus is that the deposits of the Republic (Mstislav, Horikhivs'ke) are located in complex geological conditions and characterized by a low nutrient content (5–12 wt % as P_2O_5). In this regard the technology was originally developed for the use of apatite concentrate supplied by the Russian company "Fosagro" i.e. Kirov apatite concentrate. However, the reserves of this field are significantly depleted, so since 2005 the enterprise has faced the problems related to a continuous rise in prices for phosphate raw material and difficulties in ensuring its supply. This is due to a significant decline in the quality of processed ore. So, from 1968 to 1998, the average content of P_2O_5 in the phosphate ore in Kirov deposits decreased from 18.01 to 14.39 wt. %, which in its turn, led to a reduction in the phosphorus recovery rate for the commercial product by 4%, a sharp increase in flow rate of the flotation reagents by 3.5 times [1].

This situation demanded seeking other suppliers of phosphate raw materials, one of which was the Russian company "Eurochem", which includes Kovdorsky Mining and Processing Plant (Murmansk region), which enables the production of apatite concentrates. It was planned that with the completion of a building a new enrichment plant, the company would be able to export raw phosphate to JSC "Gomel Chemical Plant". At Kovdorsky Mining and Processing Plant the acting capacity for the production of apatite concentrate containing 38 wt. % of P_2O_5, by 2010 had amounted 2.4 million tons,

and from 2025 to 2050, the capacity will decline and will be only 1.8 million tons per year.

In 2011 JSC "Gomel Chemical Plant" once again faced a shortage of supply of phosphate raw materials from Russia, that is why for loading of production capacities, a number of contracts for the supply of raw materials from Morocco, Jordan, Syria and Kazakhstan were signed. Furthermore, the delivery options of phosphate raw material from Venezuela, Vietnam and some African countries and the countries of South-East Asia are being worked out.

All of the above allows to conclude that at this stage it becomes necessary to expand the phosphate raw material base by engaging new deposits in the processing of phosphates, that is one of the urgent tasks of both Belarusian and Russian producers of phosphorus fertilizers. The assessment of the technical and economic feasibility of involving low-grade phosphate raw materials in industrial processing is not a less urgent issue.

As the experience of "Gomel Chemical Plant" showed, the transition to other sources of raw materials is not a purely technical procedure and is associated with a need for a significant change of the whole technological regime and in some cases leads to severe emergencies and elimination of production. The staff of the Department of technology of inorganic substances and general chemical technology under the order of "Gomel Chemical Plant" made a series of studies on the determining of impact of species phosphate raw materials on the technological process and techno-economic indicators of obtaining extraction phosphate acid and complex fertilizers.

Main part. The apatite concentrates of the Kirov and Kovdorsky deposits, North African phosphates deposits of Algeria, Morocco and Tunisia, as well as the Middle East phosphorite deposits of Jordan and Syria were the objects of study.

The samples of phosphate ores were investigated by X-ray diffraction and infrared spectroscopy. X-ray diffraction analysis was performed with the

use of X-ray diffractometer D8 Advance (firm Bruker), IR spectra were recorded on a FT-IR spectrometer NEXUS company NICOLET (USA) in the range of 300–4000 cm^{-1}.

As the results of the research showed, the main phase of all the samples is phosphate fluorine apatite, in some samples fluorine or fluorine hydroxy-apatite or fluorine hydroxy carbonate-apatite may be present. These apatites are close by X-ray data and explicitly are not identified by X-ray analysis. The presence of the Kirov and Kovdorsky apatites in the IR spectra and also phosphorite from Morocco at 3540 cm^{-1}, characteristic of the valence fluctuations of the OH group indicates the presence of hydroxy-apatite, although the presence of other minerals containing hydroxy-group is also possible. The IR spectra of all the phosphates have bands of varying intensity and forms in the range of 1430–1460 cm^{-1}, characteristic of the valence fluctuations of the carbonate ion. According to the structure, these bands are somewhat different from the bands present in the IR spectra of dolomite and calcite, and close to bands present in the IR spectra of carbonate-apatite, which allows us to make conclusions about their presence.

On the basis of X-ray diffraction and IR-spectroscopy as well as the results of chemical analysis balances were performed by cations and anions based on their charge and the phase composition of investigated natural phosphates was calculated.

The calculation method applied to the Kirov apatite is shown in Tables 1–3. In particular, a chemical amount of elements (Table 1) and corresponding to them charges of ions the presence of which is most likely (Table 2), were calculated according to the chemical analysis data. When calculating the number of components and the phase content, the unrounded values of molar masses were used. The number of significant figures was determined by the value of the component amount, the content of which in the sample is minimal, and the components remaining in excess or deficiency when calculating the phase content. In this example, the total charge of cations exceeds the total charge of anions by a certain amount Δ, which, in its turn, indicates the possible presence of an equivalent quantity of OH ions in the form of constitutional water being a part of the basic salts.

From the ratio of the elements present in the largest amount (Ca, P, F), we can assume that the main phase of this phosphate materials is fluoro-apatite. At the same time, a higher ratio P : F, and Ca : F in comparison with fluoro-apatite indicates the possible presence of chlorine and hydroxy-apatite or their mixtures. The ratio Ca : P is slightly less than that of apatite, therefore the presence of other calcium-containing phases is unlikely, however, it does not exclude the presence of

small amounts of other phosphorus-containing phases.

Table 1

Results of calculation of the amount of the chemical component

Chemical analysis results per elements or oxides		Calculated data of the chemical amount of component	
component	wt. %	component	mol
H_2O	0.22	–	–
P_2O_5	39.16	P	0.55177
CaO	50.32	CaO	0.89733
MgO	0.09	MgO	0.00223
F	3.27	F	0.17212
Fe_2O_3	0.54	Fe	0.00676
Al_2O_3	1.63	Al	0.03197
SO_3	0.10	SO_3	0.00125
SiO_2	1.00	SiO_2	0.01664
CO_2	absent	–	–
K_2O	0.032	K	0.00068
Na_2O	0.29	Na	0.00936
Cl	0.16	Cl	0.00451
H.o.	0.19	SiO_2	0.00316
Σ	97.00		
Σ	96.18		

The calculation of the amount of the presumed phase was carried out in most cases on the component present in a lack/negative, considering that the excess or lack of other components was minimal. The excessive number of remaining components was used to calculate other phases. By reducing the excessive amount of remaining components to values not exceeding 0.5% in terms of oxide, the calculations were completed.

In this example (Table 3) the amount of the main phase of $Ca_5(PO_4)_3F$, calculated by fluorine, is 0.17212 mol. The excess of the remaining components makes: phosphorus – $0.55177 - 0.17212 \cdot 3 = 0.03541$ mol, calcium – $0.89733 - 0.17212 \cdot 5 = 0.03673$ mol. The amount of the next phase of $Ca_5(PO_4)_3OH$, calculated by the remaining excess of calcium, is $0.03673 : 5 = 0.00735$ mol. The excess of phosphorus amounts $0.03541 - 0.03673 \cdot$ $0.6 = 0.01337$ mol. Next, the content of possible impurities was calculated: aegerite $NaFe(SiO_3)_2$, nepheline $(Na,K)AlSiO_4$, quartz, alluminium phosphate. The amount of quartz was taken equal to the amount of insoluble residue per SiO_2. The amount $(Na,K)AlSiO_4$, calculated on the sum of sodium and potassium is 0.01004 mol. Thus, aluminium and silicon: Al – in the amount of $0.03197 - 0.01004 = 0.2193$ mol, Si – in the amount of $0.01664 - 0.00316 -$

– 0.01004 = 0.00344 mol, are in excess. The amount of $NaFe(SiO_3)_2$ – 0.00344 : 2 = 0.00172 mol was calculated by this excess of silicon. Although the entire amount of sodium was used in a previous calculation of the phase, its disadvantage per oxide is a small quantity – 0.05%. The excess of iron is 0.00676 – 0.00172 = 0.00504 mol. The content of $AlPO_4$ was calculated by the excess of phosphorus equal to 0.01337 mol. Aluminium is then in excess 0.02193 – 0.01337 = 0.00856 mol. The content of the remaining components is less than 0.5% per oxides. The deviation of the total content of the phases from the sum of the initial components amounted about 2%, which is acceptable to the calculating.

To identify and calculate the content of impurities, except for the data of chemical and X-ray analyzes, the literature data were used for further studies, since due to the low intensity of the reflections of impurities on radiographs, we can only speak about the probability of the presence of the individual phases. Impurities, including components in the amount of less than ~0.5%, were not taken into account in the calculation of the composition of all samples.

Full deciphering of the radiographs (description of the phases) was performed using the database of JCPDS International Centre for Diffraction Data. On the basis of the obtained data on the phosphate raw material composition and calculated material balances it was possible to analyze the impact of various types of phosphate raw materials on the technological process of phosphoric acid and complex fertilizers production (Table 5).

Table 2

Results of calculation of the balance of ionic charges

Cations		Anions	
component	mol	component	mol
Ca^{2+}	1.79466	PO_4^{3-}	1.65531
Mg^{2+}	0.00446	F^-	0.17212
Fe^{3+}	0.02028	SO_4^{2-}	0.00250
Al^{3+}	0.09591	SiO_3^{2-}	0.03328
K^+	0.00068		0.02696
Na^+	0.00936	Cl^-	0.00451
Σ	1.92535	Σ	1.86140
		Δ	0.06395

Δ = OH; per H_2O 0,031975 mol, or 0,58 wt. %

	Options	
instead SiO_3^{2-} SiO_4^{4-} without undissolved residue	0.06656	
	0.05392	
Σ (without undissolved residue)	1.88836	
Δ	0.03699	

Δ = OH; per H_2O 0.01850 mol, or 0.33 wt. %

Table 3

Results of calculation of the phase content

Phase	The content of the phase			Excess or lack (–) of the component		
	calculated by the component	mol	wt. %	component	mol	wt. % per oxide
$Ca_5(PO_4)_3F$	by F	0.17212	86.80	P	0.03541	–
				Ca	0.03673	
$Ca_5(PO_4)_3OH$	by excess of Ca	0.00735	3.69	P	0.01337	–
$(Na, K)AlSiO_4$	by Na and K	0.01004	1.44	Al	0.02193	–
				Si	0.00344	
$NaFe(SiO_3)_2$	by excess of Si	0.00172	0.40	Na	–0.00172	–0.05
				Fe	0.00504	0.4
SiO_2	by undissolved residue	0.00316	0.19	–	–	–
$AlPO_4$	by excess of P	0.01337	1.63	Al	0.00856	0.44
Total			94.15			

Table 4

Phase composition of the investigated natural phosphates

Phosphate raw material	Main phases	Impurities phases
Apatites		
Kirov apatite	Fluorapatite, hydroxy-apatite (fluoro hydroxyl-apatite)	Nepheline, aegirine, silica, aluminium phosphate, feldspar, sphene
Kovdorsky apatite	Fluorapatite, hydroxy-apatite, carbonate apatite, (fluoro hudroxycarbonate apatite)	Dolomite, calcite, silica, magnesium hydroxy-silicates, fluorine
Phosphorites		
Algerian phosphorite	Fluorapatite, carbonate apatite, (fluoro hudroxycarbonate apatite)	Calcite, dolomite, gypsum, fluorite, aluminium silicates of sodium-potassium, silica, feldspar, glauconite
Moroccan phosphorite	Fluorapatite, carbonate apatite, (fluoro hudroxycarbonate apatite), quartz	Gypsum, calcite, dolomite, fluorite, calcium silicates
Tunisian phosphorite	Fluorapatite, carbonate apatite, (fluoro hudroxycarbonate apatite)	Calcite, dolomite, silica, fluorite, aluminium silicates of sodium-potassium, glauconite, aegirine, feldspar, calcium
Jordan phosphorite	Fluorapatite, carbonate apatite, (fluoro hudroxycarbonate apatite), quartz	Calcite, gypsum, fluorite, aegirine, calcium silicates
Syrian phosphorite	Fluorapatite, carbonate apatite, (fluoro hudroxycarbonate apatite), quartz	Calcite, dolomite, gypsum, fluorite, calcium and magnesium silicates

The data on the main technological parameters of the production of phosphoric acid in the transition to alternative types of phosphate raw materials [2, 3] led to the following conclusions:

– the transition to alternative types of raw materials leads to a significant increase in the amount of pulp allocated to a filtration step (per 500–630 kg of pulp per 1 ton of phosphate raw material or per 20–25 tons/hour), and increase on burden on filters; besides, when performing the calculations, we did not take into account the significant deterioration of rheological and chemical-technological properties of the resulting (in the extraction step) suspensions in the extraction step (viscosity, fluidity, filterability) due to the high content of magnesium compounds and silicon sodium fluoride, silicic acid gel formation, so the practical indicators of the filtration process in the transition to alternative types of raw materials will be significantly lower;

– the increase in the amount of circulating pulp fed to the extractor, in the transition to alternative types of raw materials 5 tons per 1 ton of phosphate raw material (or up to 200 tons per hour), which, taking into account the average specific weight of the pulp of 1.5 t/m^3, is 133 m^3; thus increasing the amount of the circulating pulp, the extractor useful volume is reduced by 15%;

– a significant reduction of the amount of the emitted fluoride compounds into the gas phase by 1.5–2 times during the decomposition (from 21.07 to 9.72 kg per 1 ton of phosphate raw material) causes the reducing of the amount of emitted fluorine at the stage of the absorption purification and as a result, reducing the amount received in the form of salable products of fluoro salts. Besides, the lack of fluoride leads to the unbalance of F : SiO$_2$ ratio in the extraction pulp, increase in the number of free (unbound) silicic acid and further deterioration of the filtering process and evaporation (in the form of deposits on pipes, gas flues and heating surfaces);

– the reduction of the concentration of product acid from 32 to 25–27%, as well as the increase in the mass of evaporated water is the cause of increasing energy consumption during a subsequent evaporation and processing of product acid in the manufacture of complex fertilizers on the basis of ammonium phosphate.

The presence of carbonates in the composition of carbonate apatites, fluoro hudroxycarbonate apatites, dolomite, calcite in the alternative types of phosphate raw material leads to the emission of a significant amount of carbon dioxide at the stage of decomposition (from 26 to 39 kg of CO$_2$ per 1 ton of phosphate raw material or up to 1.04–1.56 tons per hour), resulting in excessive foam formation in the extractor. Due to the abundant foaming through carbon dioxide emissions when using alternative types of phosphate raw material, the practical volume of the reaction mass in the extractor (pulp) should be reduced by 25–40%, because the existing in the workshop extractor CTF-1 will not provide the required capacity, or it is necessary to reconstruct the workshop with the installation of a new extractor of the required volume and a filter with a large filtering surface;

– the estimated power reduction for product acid ranged from 8.66 to 27.21% (depending on the type of alternative raw material) and the consumption rate of phosphate raw material increased from 2.804 (for the Kirov apatite) to 3.07–3.852 t/t, which in its turn leads to a significant reduction in the amount of the obtained phosphoric acid to 20,000–30,000 tons P$_2$O$_5$ per one typical process thread.

Table 5

**Data on production capacity of EFK in the transition
to alternative types of phosphate raw materials**

Type of phosphate raw material	Consumption of raw phosphate (nature) per 1 ton of product acid (100% P_2O_5), t / t	Reduction capacity for product acid (100% P_2O_5) in processing 1 ton of phosphate raw material, %	Productivity of the workshop of phosphotic acid (at the same flow rate of phosphate raw materials) in terms of tons of P_2O_5, t / year	Consumption of phosphate raw materials, t / h	The relative decrease in performance at the maximum load recorded for raw phosphate, %	Productivity of the workshop of phosphotic acid (typical process thread) in terms of tons of P_2O_5, t / year
Workshop of phosphoric acid of the 1 st turn JSC "Gomel Chemical Plant"						
Kirov apatite	2.645	100	110,000	46	0	110,000
Kovdorsky apatite	2.914 (+0.269)	90.78 (−9.22)	99,858	40	−13.04	86,833
Syrian phosphorite	3.520 (+0.875)	75.16 (−24.84)	82,676	31[*]	−33.33	55,716
Tunisian phosphorite	3852 (+1.207)	68.67 (−31.33)	75,537	31[**]	−33.33	50,905
Algerian phosphorite	3.922 (+1.277)	67.45 (−32.55)	74,195	31[**]	−33.33	50,001
Jordanian phosphorite	3.383 (+0.738)	78.2 (−21.8)	86,020	31[**]	−33.33	57,970
Kirov apatite (50%) + Syrian phosphorite (50%)	3.14 (+0.495)	84.24 (−15.76)	92,664	39	−15.21	78,562
Kirov apatite (80%) + Syrian phosphorite (20%)	2.952 (+0.307)	89.61 (−10.39)	98,571	39	−15.21	83,571
Kirov apatite (70%) + Kovdorsky apatite (30%)	2.874 (+0.229)	92.06 (−7.94)	101,266	40	−13.04	88,057
Kovdorsky apatite (80%) + Algerian phosphorite (20%)	3.096 (+0.451)	85.46 (−14.54)	94,006	40	−13.04	81,744
Kirov apatite (50%) + Algerian phosphorite (50%)	3.327 (+0.682)	79.5 (−20.5)	87,450	40	−13.04	76,043
Kovdorsky apatite (70%) + Syria 70/30	3.070 (+0.425)	86.16 (−13.84)	94,776	39	−15.21	80,354
Kovdorsky apatite (40%) + Morocco 40/60	2.971 (+0.326)	89.03 (−10.97)	97,933	42	−8.7	89,417
Workshop of phosphoric acid of the 2nd turn JSC "Gomel Chemical Plant"						
Kirov apatite	2.645	100	86,087	36	0	86,087
Syrian phosphorite	3.520 (+0.875)	75.16 (−24.84)	64,703	24	−33.33	43,135
Moroccan phosphorite	3.095 (+0.45)	85.48 (−14.52)	73,587	36	0	73,587

[*] In the transition from the Kirov apatite to Syrian phosphorite, according to a survey of central plant laboratory JSC "Gomel Chemical Plant", the drop of feed (consumption) of raw materials due to the high content of CO_2 (3.25%) was 33.33%.

[**] The consumption of phosphorites from Tunisia, Algeria and Jordan is accepted similar to that of Syrian phosphorites, as these sources of phosphate raw materials are characterized by a high content of CO_2 (from 2.08 to 6.32%).

Conclusion. The comparative analysis and calculation of the technological indices of production EFK during the transition to alternative forms of phosphate raw materials based on the calculation of the number of gypsum data and output values of phosphorus-gypsum per 1 ton P_2O_5 in production phosphoric acid confirmed the reduction of product acid capacity to 25% even in the case of presence an extractor of a required volume (including the foaming process), and providing the necessary space (capacity) for filtering.

References

1. Смирнов, Ю. М. К вопросу модернизации производства хибинского апатитового концентрата / Ю. М. Смирнов // Хим. пром-сть. – 2001. – № 9. – С. 12–15.

2. Дыбина, П. В. Расчеты по технологии неорганических веществ / П. В. Дыбина, А. С. Соловьева, Ю. И. Вишняк. – М.: Высш. шк., 1967. – 524 с.

3. Позин, М. Е. Расчеты по технологии неорганических веществ / М. Е. Позин; под ред. проф. М. Е. Позина. – Л.: Химия, 1977. – 496 с.