Chapter 2
Print ISBN: 978-81-19761-95-1, eBook ISBN: 978-81-19761-39-5

Phosphates of Ukraine as Agrochemical Raw Materials

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DOI: 10.9734/bpi/cicms/v1/1066G

ABSTRACT

The aim of the article was to analyze the available resource potential of phosphate raw materials in Ukraine and determine their suitability for application in agrochemistry, particularly for the production of mineral fertilizers and ameliorants. The article analyzes the present state of the phosphate raw material base to meet Ukrainian chemical enterprises' needs. In Ukraine, a number of complex apatite and phosphorite deposits have been explored. Their exploitation can lead to a complete supply of Ukrainian chemical enterprises with raw materials and can partly reduce the amount of expensive imported phosphate mineral fertilizers. At present, the following deposits, where apatite is connected with other useful components, are prepared for exploitation: Stremyhorod, Fedorivka, Novopoltavka, Kropyvna and others. The advantage of the development of these deposits is the possibility to extract apatite along with the production of rare earth concentrates, ilmenite, titanomagnetite, as well as feldspars, olivine, pyroxenes, mica and others which will significantly increase the profitability of the deposit's development.

The alternative to apatite-containing deposits in Ukraine can be sedimentary deposits of nodule, granular and mixed type phosphorites. Phosphorite deposits can be used mainly for the production of phosphorite and limestone flour. Considerable resources of granular phosphorites have been discovered in Volyn-Podillia and Dnieper-Donetsk which are considered to have a various agricultural effect. They are environmentally friendly ores without impurity which prevents plants from cesium, strontium and reduces nitrates in the soil. Arranging the exploration of phosphorite ores in certain parts of Volyn-Podillia basin and Dnieper-Donets Rift is recommended.

Keywords: Apatite ores; phosphorite ores; resources; deposits; raw materials.

1. INTRODUCTION

The first specialized publications on the phosphorites of Podillya, concerning their geological exploration and properties, appeared in Austrian and Russian

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journals in 1869. They were presented almost simultaneously by M. Barbott-de-Marni, A. Alt, and E. Glazell. In addition to the mentioned authors, in the second half of the 19th century, Podillya's phosphorites were described by F. Schwakhofer [1], N. Gunn [2], F. Benyash [3], E. Dolinsky [4], E. Dunikovsky [5], F. Roemer [6], O'Relli [7], and others.

Geological studies of Podillya's phosphorites, their composition, and properties led to the beginning of their intensive exploitation for agricultural purposes. Development of deposits started in the mid-19th century and continued until its end when the main reserves of known deposits were practically exhausted. All deposits were located in the basins of the left tributaries of the Dniester River – Ushytsya, Kalyus, Zhvana, and Lyadova.

Of particular interest are the works of the well-known Ukrainian geologist V. Chyrvinskiy [8,9], in which the chemical and mineralogical composition of Podillya's phosphorites is examined. Certain interruptions in the systematic studies of Podillya's phosphorites were associated with the events of the First World War and the 1917 revolution, which affected the territory of Podillya. It was only in 1921 when the newly formed South-Western Industrial Survey Administration resumed work under the general supervision of V. Luchytskyi. The results of these investigations were published between 1923 and 1925. In 1925, R. Vyrzhikivskyi [10,11] continued the research on phosphorite deposits in the Ushytsia River basin. Several publications by this author, describing individual phosphorite deposits, were published between 1930 and 1936. In the late 1920s, researchers from the Institute of Fertilizers – N. Zonov, I. Kurman, and N. Larin "On the formation of Podillia deposits of phosphorites" (1932) – conducted works in the Dniester region. They developed a stratigraphic scheme of Paleozoic deposits in the Ushytsia River basin and later, for the entire phosphorite-bearing area.

In 1944, based on the map of mineral resources he compiled, L. Tkachuk identified prospective areas of phosphate deposits in the Dniester region. In the 1960s, three significant monographs were published, providing comprehensive coverage of the issue of phosphorite-bearing regions in Podillya. These works include the research by D. Kovalenko, V. Semenov, titled "Phosphates of Ukraine" (1964), Y. Lazarenko and B. Srebrodolsky's "Mineralogy of Podillya" (1969), and Y. Lazarenko and D. Kovalenko's "Agronomic Ores of Ukraine" (1966). Finally, in the 1980s, works by Y. Senkovskyi and A. Senkovskyi presented modern conceptions of the geological structure and genesis of phosphorite deposits in the Volyn-Podillya region. Primarily, this includes A. Senkovskyi's dissertation "Geology of Cretaceous Phosphorites of the Volyn-Podillya Periphery of the East European Platform" (1984) and the comprehensive work by Y. Senkovskyi and V. Hlushko titled "Phosphorites of Western Ukraine" (1989).

In the last decades, the issue of phosphate raw materials in Ukraine has been examined from various perspectives by authors such as Yu. Bragin and D. Bragin [12,13], M. Syvyi [14], V. Havryluk [15], I. Shepel and I. Klymenko [16],

O. Dubyna [17], O. Melnyk [18], G. Rudko [19], M. Syvyi and P. Demyanchuk [20], and others.

Ukraine is a consumer of phosphate and complex phosphorite mineral fertilizers, however the extraction of raw materials and production of phosphate fertilizers and ameliorants is done in small amount. At present, Ukraine produces phosphate fertilizers at only two enterprises: Public Joint-stock Company (PJSC) “Sumykhimprom” and PJSC “Dniprovskiy Plant of Chemical Fertilizer” that has a total production capacity of 1434 thousand tons 100% P_2O_5 in the form of complex mineral fertilizers. PJSC “Crimean TITAN” is located on the territory of the annexed Crimea and is not actually controlled by Ukraine.

Due to the termination of supplies of Khibiny apatites from the Russian Federation, Ukraine faced the challenge of providing fertilizer production plants with phosphate raw materials. Initially, it was supplied from Syria, but later the supply (mainly phosphorites) was redirected to countries in North Africa and the Middle East. However, as of January 1, 2021, Ukraine has explored and accounted for 7 apatite deposits (including 5 complex deposits) with industrial reserves of 71,911 thousand tons of P_2O_5 and 9 phosphorite deposits (including 4 complex deposits) represented by phosphatic iron ores (3 accounting objects), granulated phosphorites (2 deposits), yellow phosphorites (1 deposit, 1 accounting object), and phosphorite-glauconite ores (2 deposits) with industrial reserves of over 11,090 thousand tons of P_2O_5 [10]. Among these, 6 deposits were under development or received permits for industrial development in 2021, but actual extraction data is not publicly available. Therefore, the actual production of phosphate fertilizers is carried out almost exclusively by means of imported raw materials supplies. Explored complex apatite deposits require a significant in- vestment to start to be developed. Phosphorite concentrates and mineral fertilizers produced from them are of lower quality than those made of apatite and will obviously be consumed only within the country. The use of low-grade phosphate raw materials has, in recent years, generally become a global trend. The mentioned facts explain the importance of the immediate industrial reanimation of the phosphorite deposits as the source of the phosphate raw material industry. Current tasks are to carry out a geological and technological re-estimation of traditional phosphorite ore deposits and an evaluation of the new geological and industrial ones in order to process them into soluble mineral fertilizers. In Ukraine, the quality of the ore from the explored deposits is considered to be low and ores require special processing methods.

The aim of the article is to analyze the existing deposits of phosphate raw materials in Ukraine, to define their ability for industrial use, to suggest ways of their efficient use and expansion of the raw material base for supplying local chemical plants for the production of modern phosphorus and complex mineral fertilizers which would prevent (at least partly) from expensive imported phosphate transportation.

In Ukraine, resources of phosphate raw material are represented mainly by deposits of apatites, phosphorites and glauconites.

2. APATITE RAW MATERIALS

Four main genetic types are distinguished among the deposits of apatite ores which are the main raw material base for the production of traditional mineral fertilizers (superphosphate, ammophos etc.): magmatic, metamorphic, carbonatite and weathering crust. In Ukraine, all geological and industrial types of deposits are found. seven deposits of complex apatite-ilmenite ores are listed in the state balance of reserves: Kropyvna, Stremyhorod, Torchyn, Fedorivka (Zhytomyr oblast) and Nosachiv (Cherkasy oblast) (Table 1) where apatite is considered as a supplementary raw material, as well as two deposits of apatite-ilmenite ores – Davydky (Zhytomyr oblast) and Novopoltavka (Zaporizhia oblast), where apatite was defined as the main mineral resource. At present, none of the deposits are being developed.

The magmatic type is represented by deposits in Stremyhorod, Fedorivka, Nosachiv and others are related to Korosten and Korsun-Novomyrhorod pluton of the Ukrainian shield and associated with the formation of gabbro-anorthosites. They contain complex ilmenite-apatite-titanomagnetite ores. In the weathered crust of the Gabroids occur residual and infiltrational type deposits of apatite-ilmenite ores of industrial value. The P_2O_5 content of such ores ranges from 0.01 to 5.8%.

On the basis of *Stremyhorod* apatite-ilmenite deposit located near the Irshansk Mining and Processing Plant, it is possible to establish an enterprise with an annual production of 860 thousand tons of apatite concentrate with a P_2O_5 content of 38%. Ores are easily enriched with the simultaneous release of ilmenite, apatite and titanium-magnetite concentrates of high quality. A special permit for resource use in Stremyhorod deposit, 20 kilometers from the village Irshansk, was obtained by LLC “Valki Ilmenite” in 2012.

The *Nosachiv* deposit of apatite-ilmenite ores of the Korsun-Novomyrhorod pluton was transferred to “Tiofab” Ltd. for exploitation (2007). The deposit has a similar mineral con- tent as the well-known Telnes ilmenite deposit in Norway, Rogaland province (without or with little magnetite). The technological features of the ores from the Nosachiv deposit are similar to the ores of Stremygorod and Fedorivka deposits, but they are considered to be technologically better and easily enriched. The ores can be processed by the technologies used at these two deposits, but fewer operations are required.

According to the developed beneficiation technology, obtaining apatite concentrate containing P_2O_5 of not less than 39% is planned. Apatite concentrate is a substance rich in phosphorus and fully meets the requirements of the European Economic Association concerning the production of phosphate fertilizers. The expected total cost of the ore mining and processing plant for the development of Nosachiv deposit will be [17], approximately, about USDUSD 250 million and the period of the plant construction with its full production capacity will be up to 5 years.

Table 1. Resource base of apatite ores of Ukraine

Oblast	Deposit name	Type of deposit	Type of ore	Mineral resources ($A+B+C_1+C_2$) thousand tons P_2O_5 thousand tons	Average P_2O_5 content in ore [%]
Cherkasy	Nosachiv	1) magmatic	apatite-ilmenite	359714/43966	No information
Zhytomyr	Stremyhorod	2) weathering crust of the Gabroids	apatite-ilmenite	886344/23688	2.4
	Fedorivka		apatite-ilmenite titanomagnetite,	129776/3919	3.0
	Davydky		apatite-ilmenite	57022/2069 (C_1+C_2)	3.63
	Kropyvna		apatite-ilmenite titanomagnetite,	221730/5419 (C_1+C_2)	2.15 (1.8–2.45)
	Torchyn		apatite-ilmenite	209090/696	0.3
Zaporizhia	Novopoltavka	1) carbonatite 2) weathering crust and carbonatite	apatite- -rare-metals	859623/46578	4.9
Total:				2363585/126335	–

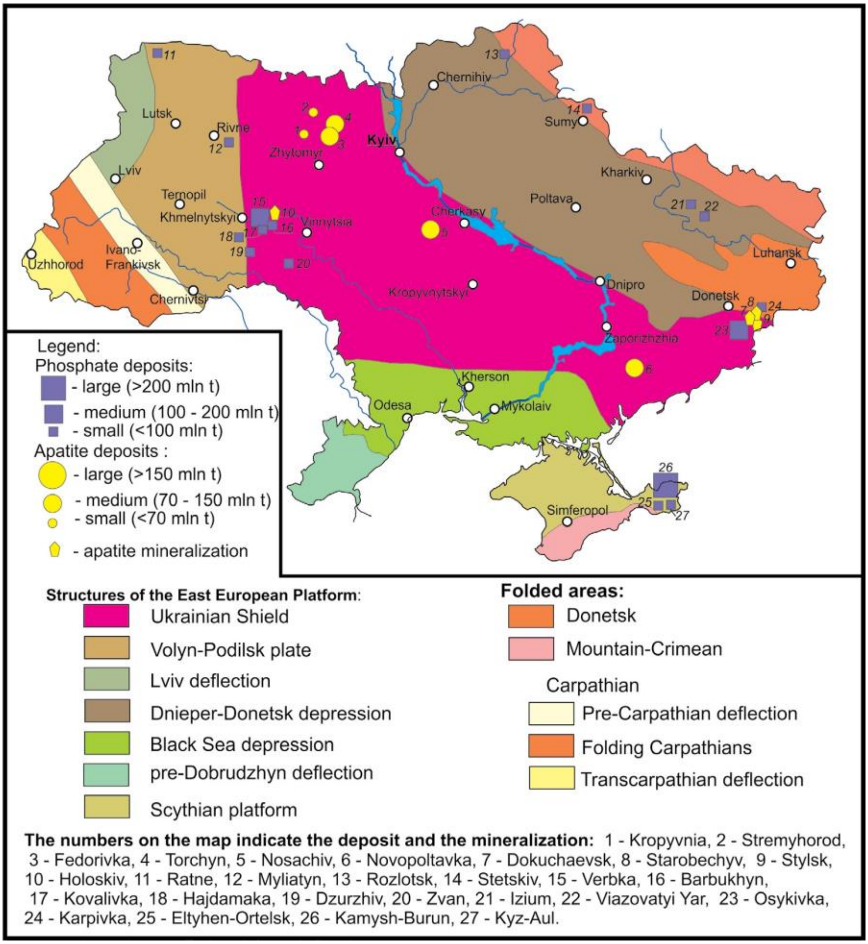

Fig. 1. Occurrence of resources of phosphate raw materials in Ukraine

The geological and economic estimation of the southern part of *Davydky deposit* of ilmenite apatite ores in Narodychiv district of Zhytomyr oblast has revealed the reserves of bedrock ores in the categories C_1+C_2 in the amount of 57022 thousand tons with the average P_2O_5 content of 3.63% and TiO_2 – 5.53% (Table 1). The general off-balance inferred resources of C_2 category ar 47 243 thousand tons with an average P_2O_5 content of 1.13% and TiO_2 – 6.31%. According to the technical and economic calculations [18], the index of cost-effectiveness to the cost price is estimated as 16.4%, the payback period of the primary investments is 9.9 years, the index of profitability is 1,007, the index of the enterprise profitability is 0.274. However, the State Service of Geology and Subsoil of Ukraine has canceled the special permit for a private enterprise "DBR-3" to extract ilmenite-apatite ores from the southern part of Davydky deposit due to their refusal to pay the state budget for the permit to use the resources. Therefore, now the deposit is expecting its investor.

According to the exploration data of the *Kropyvna deposit* [22], which is located in Volodar-Volynskyi district of the Zhytomyr oblast and is related to bedrock-ultrabasic intrusion, two types of ores are distinguished: the weathering crust and bedrock, which, consequently, make up two ore bodies. Mining, engineering, geological, hydrological and hydrogeological conditions of the deposit are favorable for opencast mining. The ore reserves will provide ore for the mining company with a capacity of 12,000 thousand tons per year for a period of 18.4 years. The deposit is completely prepared for industrial mining even in uncertain economic conditions. In 2007 the gas trader “Sirius” received a permit to mine the Kropyvna deposit. The deposit is located fifteen kilometers from the Irshansk Mining and Processing Plant. It claimed the need of USD 2.2 billion investment [23]. The company promises to invest USD 230–250 million in the mining at the first stage. The money should be spent on building a mining and processing plant with an annual capacity of 12 million tons of ore. The production of titanomagnetite concentrate will make 1.68 million tons of ilmenite concentrate – 0.3 million tons and of apatite concentrate – 0.66 million tons.

In addition to the mentioned above, a number of previously evaluated deposits in the Irshansk mining region within the boundaries of the Ukrainian Shield are defined, particularly deposits in: Vydybor, Paromiv, Yuriv, Slavechne. More than 10 potentially valuable ore occurrences were discovered. The total resources of P_2O_5 in the mining industry are 258 million tons with P_2O_5 content of 3–10% in the ore [13].

In the Archean plagioclase-pyroxene crystalline shale near the village Tropove of the Mohyliv-Podilskyi district (Vinnytsia oblast), the occurrence of large apatite impregnation has been revealed. A group of steeply falling ore bodies (each of 30–40 m thick) was found in wells with the thickness of 60–300 m. The content of P_2O_5 in the bodies varies from 2.0–4.2%. The total projected resources are estimated at 20 million tons.

The apatite occurrence in the crust of weathering of serpentinites with the apatite content of 20–30 kg/t are found in the Khmilnytsk district of the Vinnytsia oblast.

Carbonatite ores are represented by the deposit in Novopoltavka (Fig. 2) and the ore exposition of Pre-Azov area, Proskuriv and other potentially valuable massifs of Podillia. Particularly, in the Letychiv district of the Khmelnytskyi oblast within the Holoskiv apatiteous area, the potential exposition of apatite ores with projected resources of 30 million tons of P_2O_5 are identified. The examples of such deposits can be a number of unique apatite deposits in Russia (Khibiny, Kovdor) and Canada (Cargill, Martinson).

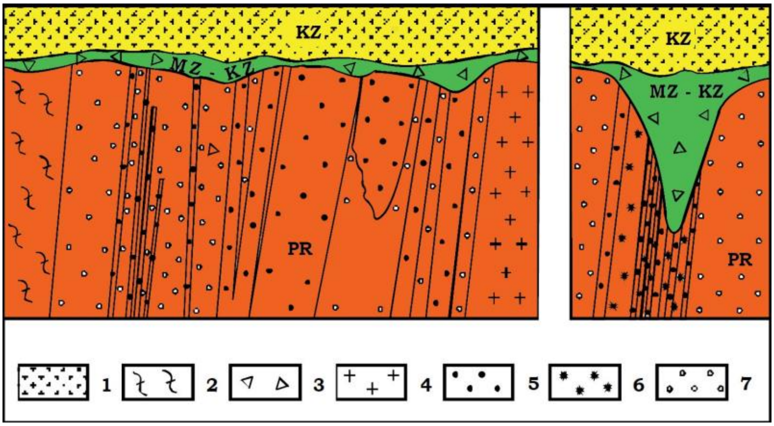

Fig. 2. Novopoltavka deposit (schematical geological section) [24]
1 – loam, clay, sand; 2 – migmatite, gneiss; 3 – weathering crust; 4 – granitoid; 5–7 – apatite rocks: 5 – carbonate; 6 – albitite; 7 – syenite; PR – primary ore, MZ – residual and infiltration type ore, KZ – overburden

In 1990, the feasibility study of the construction of an underground mine and a concentrating mill near the _Novoplotavka deposit_ of apatite-rare-metals ores was carried out. The practically wasteless apatite ores processing technology enables up to 1650 thousand tons of apatite concentrate with the content of anhydride of phosphoric acid of 38% per year to be received. The development of the Novopoltavka deposit alone can fully supply Ukraine with apatite and such rare metals as: Nb, Ta, Ce, La, Nd, Sr for the next 25–50 years. The concentration of rare metals in rare earth apatites can reach 11% of TR_2O_3. In addition, fluorine can simultaneously be extracted from the apatite which contains a high content of this mineral (up to 3,3% F). It is also possible to obtain 1.45% of rare earth elements in the ore enrichment process, which significantly increases the profitability of the development of the deposit. The rare earths extraction from apatite can completely cover the costs of the deposit development [6]. The “Volyn Mining and Chemical Company” Closed Joint-Stock Company investor is currently obtaining the approval and carrying out the examination for further exploitation of the deposit.

3. PHOSPHORITE RAW MATERIALS

In Ukraine, the deposits of ores that contain phosphorite are widespread within the Volyn-Podillia plate, the Dnieper-Donets rift, the north-eastern slope of the Ukrainian shield, the southwestern slope of the Voronezh crystalline massif and the Indo-Kuban trough which are connected with the deposits of Upper Precambrian (Vendian), Cretaceous, Paleogene and Neogene ages. Phosphorites are found among the layers of marls, argillites, quartz-glauconite sands, less often sandstones and limestones in the form of small nodules, pebbles. Meanwhile, the thickness of deposits varies from 0.5 to 10–15.0 m, and the content of P_2O_5 in the ore can be from 4.0 to 50.0%.

According to the mode of occurrence of the phosphate component, Ukrainian phosphorites are divided into nodular, granular, mixed-type and brown iron ore phosphorite. The first three types are the most widespread and industrially important.

Nodular phosphorites are formed of separate concretions of different sizes (1–2 to 10–15 cm) included in the rock (clay, sand, chalk, etc.) and unevenly spread in it. They are found on the territory of Middle Dniester in the form of bedrock layers and in the Volyn, Polissya, Dnieper-Donets rift in the form of redeposits [25].

Three phosphorite-bearing basins are distinguished within the southwestern part of the eastern European Platform: Podillia Vendian, Volyn-Podillia Cretaceous and Polissia Paleogene [25], another basin of Cretaceous Age – Dnieper-Donetsk – is identified on the left bank of the Dnieper river.

The Podillia Vendian basin covers the area of development of Vendian Kalus bed within the southwestern slope of the Ukrainian shield. Phosphorite content is predominantly found among the deposits of the Nahirianka Vendian formation. It is also occasionally found in the earlier deposits of this system.

The areas of occurrence of Kalus beds (mynkivets horizon) are located in the Middle Dniester, in the Dniester valley and the Dnister's left tributaries: the Zhvan, Kalus, Ushytsia, and wells are also found on the basins of the Southern Bug and Horyn. The productive horizon with the thickness of 5–25 m is composed of a monolith of dark gray or gray-green thinly layered shale argillites with interlayers of the siltstones. Phosphorites are represented by concretions of 2–25 cm in diameter. The content of P_2O_5 in bedrock phosphorites of the Kalus beds is 30–38%, consequently they can be considered high-quality raw materials to produce phosphate fertilizers – superphosphate, phosphorous flour etc.

During Cretaceous (Albian) transgression, Vendian phosphorite deposits were affected by intensive erosion and subsequent redeposition of phosphorites in shallow basins extending along the flooded southwestern part of the Ukrainian shield. Thus, the redeposited concretionary phosphorites, which were formed in this way make up the basal layer of the Mid-Upper Albian and overlaying Lower Cenomanian deposits. The latter one along with the bedrock Cretaceous phosphorite form the cretaceous Volyn Podillia Basin [25].

Phosphorite occurrence of the *Middle Albian* age described by Y. Senkovsky and others [25] is found in the Borshchiv district of Ternopil oblast in the Hudykivtsi and Pylypche villages. Productive deposits are formed by shellfish and sandy phosphorites and occasionally by pellets (round objects of 0.06–2 mm), phosphoritized wood and remnants of elasmobranchs (teeth). They form rich clusters 0.3–0.5 m thick with the phosphorite content of 40–50%. No special geological exploration on revealing the phosphorite content in the Middle Albian has been carried out until now.

In the Upper Albian horizon, phosphorites of two genetic types are present: redeposited concretions of the Vendian age and bedrock sandy nodule phosphorites.

Redeposited Vendian concretion phosphorites lie among the coarse-grained rocks (conglomerates) of Albian age and are found near the following villages: Liadova, Bernashivka, Hlybivka and others (Khmelnytskyi oblast), where they constitute a productive horizon with a thickness of 0.2–1.0 m.

According to various researchers, the resources of phosphorite concretion do not exceed 300–500 thousand tons, and the deposit productivity can be no more than 300 kg/m^2 (while earlier the productivity of these horizons was 1,000–1,800 kg/m^2). However, Y. Senkovsky and others [25] consider the territory of the plateaus between the left-hand tributaries of the Dniester to be potentially valuable for the discovery of new industrial concentrations of this type of phosphorires. However, the possibility of deposit development problematic because the productive layer lies at a depth of 100 m and can only be developed by underground mining.

Upper Albian bedrock phosphorites lie among the quartz-glauconite sands and have a good outcrop in Mohyliv Podnistrovia (Dzhyhivka, Naslavcha and others).

Next to the Zhvan village in Murovani Kurylivtsi district, a mixed-type *Cenomanian* phosphorite deposit (Zhvan deposit) was discovered in 1954 (Fig. 3). The deposit was predominantly represented by nodule and granular phosphorites of 0.1–0.5 mm – 2–5 cm and phosphorite-bearing glauconite sand and additionally by redeposited spherical concretions and their parts (Table 2).

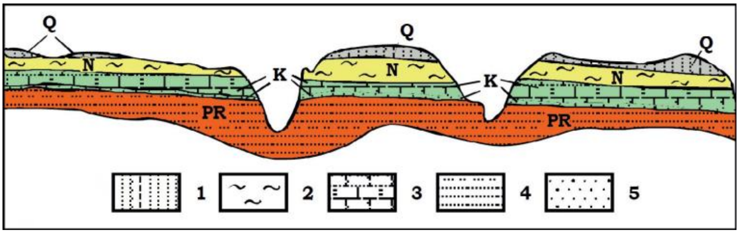

Fig. 3. Zhvan deposit (schematic geological section) [24]

1 – loam, clay, sand; 2 – clay, limestone, sand; 3 – chalk, marl; 4 – argillites, siltstone, sandstone; 5 – quartz-glauconite sandstone with pebbles of phosphorites; Q – Quaternary, N – Neogene, K – Cretaceous, PR – Precambrian

The phosphorite horizon with the thickness of 8/10–20/30 m lies at a depth of 70–100 m and reaches the surface only on the slopes of the river valleys. The thickness of the ore layer is 0.9–1.5 m. Only the reserves of the Northern section are rated C_1 category and are estimated at 752 thousand tons calculating as an enriched concentrate with a P_2O_5 content of 16%. The thickness of the ore layer is 450–470 kg of concentrate per 1 m^2.

Table 2. Phosphorite resource base in Ukraine

Deposit age	Deposit type	Mining ore type	Deposits, potential areas	Mineral resources, phosphorite ore, P_2O_5, [thousand tons]		Inferred resources P_2O_5, [thousand tons]	Content P_2O_5 [%]
				$B+C_1$	C_2	P_1	
Podillia Vendian basin	bedrock	nodular	No explored deposits	–	–		30–38
Cretaceous Volyn Podillia basin	mixed type redeposited	mixed type	Zhvan deposit, north part	10057/752	–	–	3–5
			Zozulyntsi	–	93.2	–	0.7–9.7
			Fashchivka	–	–	–	–
			Nezvysko	14700/370	4035/320	–	1.2–12.6
		granular	Myliatyn	4000/213	3583.4/247	100	6–7
			Zdolbuniv	–	–	7100	0.3–8.5
			Kopytkove	–	–	–	5.2
			Mateiky	–	–	95.6	5.9
			Bilohiria	152000	–	–	1.0–10.6
Cretaceous Dnieper- -Donetsk basin	bedrock		Karpivka	556.3/32.6	1291.5/72.6	–	5.7
			Osykove	11300/593	–	–	5.26
			Ray-Olexandrivka Zvanivka	–	–	2500	–
		nodular	Viazovatyi yar	40.6/3.66	23.2/2.3	–	–
			Synychno-Yaremovske	–	–	–	13.1 9.3

Deposit age	Deposit type	Mining ore type	Deposits, potential areas	Mineral resources, phosphorite ore, P_2O_5, [thousand tons]		Inferred resources P_2O_5, [thousand tons]	Content P_2O_5 [%]
				$B+C_1$	C_2	P_1	
			Mala Komyshuvaha				
Paleogene deposits	mixed type		Krolevets	7885/1103	–	–	13–15
	bedrock		Bantyshivka area	–	–	2700	5.0–8.14
			Dobropillia area	–	–	1000	4.1
	redeposited		Ratne deposit	–	–	8200	6.7
			Postupelska area	3500/340	–	–	9–16
Neogene deposits	bedrock	granular glauconite	Kyz-Aulske	300004/6663	–	–	2.17
			Komysh-Burunske				2.19
							2.58
			Eltyhen-Ortelske				
Man-made deposits	–	granular glauconite	Verbka	250/26.7	–	–	–

The technical and economic calculations concerning the deposit done in the 1960’s and 1990’s were based exclusively on the data of this section, though there are ore outcrops of significantly higher rates. A detailed study (exploration is currently being conducted in the deposit in the Mohyliv-Podillia and Murovani Kurylivtsi districts) may enable the areas with ore resources of 2–3 million tons to be defined [21].

Phosphorite and glauconite ores with a similar composition to Zhvan and with favorable conditions for underground mining are also found near the villages of Dzhyhivka, Rusava, and Porogiv (Yampil district). The deposits require further exploration [20,14].

In general, 8 deposits and almost 90 phosphorite occurrences were detected on a narrow area 8–18 km from the city of Yampil, Vinnytsia region, to the city of Khmelnitskyi. They are found mainly in Cretaceous sediments and are represented by nodular phosphorites of the plastogenic and organogenic structure, as well as shellfish, spongiform and phytomorphic types. In addition, there are lenses and thin layers of phosphorites containing P_2O_5 of 10–15% [26].

The preliminary exploration of the areas in Zozulyntsi in Krasyliv district and the Fashchiivka in Derazhnia district of the Khmelnitskyi oblast [21] has been completed and the resources of 93.2 million tons of ore have been found.

The Lower Cenoman phosphorite-bearing horizon appears at the ground surface between the Studenytsia and Kalius rivers and nearby areas. Here, the productive horizon is represented by quartz-glauconite and glauconite sands with a thickness of 3–6.5 m, with nodules of sandy phosphorites and concretions of brown iron ore. The content of phosphorites in sand reaches 15% and more.

In Volyn-Podillia plate occur also deposits of granular phosphorites which are the potential raw material base for phosphate fertilizer production. These are the Cenomanian phosphorites which are glauconite-phosphate-quartz sandstones on carbonate chalk cement. There are a varied types of carbonate replacement by phosphate substance (with the content of P_2O_5 from 6 to 38%) with an easily recoverable form of phosphorus oxide. The mineralogical composition of granular is: phosphorite and glauconite, phosphates, quartz, feldspars, calcite, hydromicans.

The deposits of granular phosphorites of Volyn-Podillia phosphorite-bearing basin are found within the Manevychi-Klevan and Zdolbuniv-Ternopil potential areas. The main useful mineral (phosphorite agricultural ore) is considered to be glauconite-phosphorite-quartz sand, inoceramus-glauconite-phosphorite-quartz sandstones and glauconite-phosphorite-quartz accompanying them glauconite-phosphorite sandy limestones are regarded as supplementary minerals (agricultural ore for soil deaccidation with simultaneous phosphorus enrichment).

The total thickness of deposits is up to 6 m with 250 m of overburden and up to 15% of the P_2O_5 content. In granular deposits the phosphoritized molluscs' shells-is the prevailing mode of phosphate occurrence. Prospective resources (P_2) of granular phosphorites of the mentioned above areas are estimated respectively 173.6 million tons [21].

Within the Zdolbuniv-Ternopil area, *Myliatyn deposit* (Ostroh district) is of considerable interest and is listed in the state balance of mineral reserves (Table 2). Genetically granular phosphorites of this deposit occur within marine terrigenous-carbonate deposits of the Cenomanian stage of the upper Cretaceous. The deposit can be openpit mined (the overburden thickness is not more than 12 m). It contains 247 thousand tons, inferred resources are another 100 thousand tons with 6–7% of P_2O_5 content. The experimental pilot and industrial development of the deposit is carried out by the Western Ukrainian mining enterprise. Due to the complicated mining and geological conditions of the phosphorite occurrence, specifically, high water content in the deposit forming rocks and their location on private arable lands and under built-up areas, scientists of the National University of Water and Environmental Engineering (Rivne) instead of surface mining suggested the method of well hydraulic mining, which allows the cost of exploitation to be reduced by 2–3 times along with minimizing the detrimental effects on the environment [27].

A deposit of granular phosphorites *Mateiky* is present in in the north-eastern part of Volyn oblast, on the territory of Manevychi district. Here the productive horizon is represented by fine-grained glauconite-phosphate-silica sandstone with carbonate cement. The total projected stock is 95.6 million tons of ore, or 5.9 million tons of P_2O_5 with its content of 1.1–9.5% [26].

The Upper Cenomanian phosphorite-bearing horizon in Mohyliv-Podilskyi, in Podnistrovia is defined to be connected with so-called inocerum limestone. Phosphorites in limestones occur in the form of nodule and bunchy clusters of phosphate substance (nodule sandy phosphorites), phosphatized organic fossils (sponges, shells and coprolitic phosphates, pellets), in the form of phosphate substance thinly spread in a carbonate mass that appears to impregnate the rock (phosphate limestone). The thickness of the phosphorite horizon varies from 0.2 to 3 m. The accumulation of the phosphatized fauna of the Upper Cenomanian is found near Liadova, Mohyliv-Podilskyi, Buchach and others. No exploration works on the mentioned phosphorite-bearing areas have been done yet.

Projected phosphate chalk (chalk limestone) resources in Vinnytsia Podnistrovia make up [28]: in Mohyliv-Podilskyi district – 15.9 million ton (Mohyliv-Podilskyi, Ozaryntsi and Sloboda-Yaryshkivska deposits), in Murovani Kurylivtsi district – 60 million ton (Bakhtyn and Kryvi Hyzhyntsi area).

The phosphate chalk deposits of the region occur in favorable conditions. The thickness of the overburden rock is 3.5–4.0 m, on average. In some places, they are even developed together with other chalk rocks for building needs. The possibilities of their usage are described below.

The deposit in *Osykove*, Starobeshiv district, Donetsk oblast (Table 2) belongs to Cretaceous Dnieper-Donetsk basin connected with the Kryva Luka Upper Cretaceous formation. The deposit is represented by quartz-glauconite sand overlapped by slightly phosphatous Neogene sands. The content of P_2O_5 ranges from 3 to 14% (the average is 5.2%). Stocks, calculated according to industrial categories, make up 593 thousand tons of phosphorus anhydride. The thickness of the deposit varies from 1.0 to 16.1 m, the average is 5.83 m. The average thickness of overburden rocks is 29.3 m. The south Osykove site is located in the southwestern part of the Osykove deposit where the average thickness of the overburden rocks is not more than 15 m. The area is being prepared as a local phosphate raw material base. The capacity of the occurrence ranges from 4.4 to 15 m (the average is 8.01 m) [13].

The “Donetskgeologiia” state Regional Geological enterprise began a phosphorite search and evaluation within the limits of the trough in Kryva Luka where two areas (Zvanivka and Ray-Oleksandrivka) with phosphorite rocks of Cretaceous age, have been defined. They lie under the Quaternary sediments, the thickness of which reaches 11.0 m, and in the gully, they may appear on the surface. A phosphorite stratum occurs at an angle of 30° and can be traced to the depth of 70.0 m (more than 100.0 m in some areas). The total projected resourc- es are estimated at 2.5 million tons of P_2O_5 [21].

Well-known phosphorite-bearing regions of the Upper Cretaceous age include the Izium-Donbas area located within the Kharkiv, Lugansk and Donetsk oblasts, where the deposits of Kremenets, Kryva Luka, Lysychansk, Mala Komyshuvaha, Bakhmutske, Synychno-Yaremivske are situated. Izium phosphorites are mineralogically and petrographically similar to phosphorites of the Krolevets deposit (Chernihiv oblast) as concretions are mostly sandy with P_2O_5 content of 14–19%. The recently established “Izium Phosphorites” Private limited Company began preparations for the development of the deposits of the area. It is going to process raw materials for phosphorite flour [21].

Two potential phosphorite-bearing areas of the *Paleogene age* are distinguished on the territory of the Donetsk oblast (Table 2).

Bantyshivka area is located in Sloviansk district. The sands of the middle-upper Eocene are found to be productive here. Three horizons with nodule phosphorite are distinguished. The *Dobropillia* area is located in the same district and is also connected with Eocene de- posits, represented by glauconite-quartz sand with phosphorite nodules.

In Volyn oblast*, Ratne deposit* of nodular phosphorites, redeposited from the Eocene sediments, was explored. The total projected resources are 121.6 million tons of ore, or 8.2 million tons of P_2O_5 with phosphorus anhydride content of 6.7 percent. The Postupel area where the detailed exploration (340 thousand tons of P_2O_5) was realized, has been prepared for exploitation. Nodule processing can be done in 2 possible ways:

- nodular grinding and obtaining phosphorite flour with a P_2O_5 content of 14.5% from 91.4 thousand tons directly in the quarry;
- 90.4 thousand ton of industrial nodules with the P_2O_5 content of 14.5% are sent to beneficiation plants.

The “Volyn mining-chemical company” Closed JSC received special permission (2009) for the industrial development of the field. The estimated capacity of the enterprise is 560 thou- sand tons of phosphorite flour per year [29].

In addition to the Ratne deposit, seven promising Paleogene phosphorite areas (Polissia basin) are found: Polissia, Stakhoshynska, Pivnevska, Taniushivska, Novoburlutska, Bantyshevska and Zalymanivska with a total area of 4.6 thousand square km and an estimated resources of 335 million tons of P_2O_5. The deposit parts with a thickness of more than 0.3 m and P_2O_5 content of 5% or more are considered to be potentially valuable areas [30].

The Kerch Peninsula in the Crimea is known for phosphorus-containing iron ores of the Kerch basin connected with Cimmerian deposits. The eleven deposits among which Eltyhen-Ortelske, Komysh-Burunske and Kyz-Aulske have been developed to different degrees. The total resources of iron ores and of phosphorus anhydride are presented in Table 2. The phosphorous slag produced in the process of iron ore melting (215 thousand tons/year with P_2O_5 content of 11,2% [13] was previously used as a fertilizer in the western areas of Ukraine on acid soils. Now the mining of these deposits are suspended.

A new mineral type of phosphate raw material has recently been discovered in Ukraine – *Crandallite* (Stylsko, Southern Donbass), though deposits of aluminosilicates have long been known in some countries (USA, Senegal, Russia, Kazakhstan, etc.). Crandallite mineralization in Stilsko is similar to some foreign industrial types of such ores (e.g. the Crandallite ores of Thiès deposit in Senegal contain 29% of P_2O_5). Crandallite is a complex raw material of aluminum and phosphorus, while crandallite ores can be converted into pure aluminum oxide and normal superphosphate [19].

The man-made phosphorite-glauconite deposit in Verbka (Khmelnitskyi oblast) is also listed in the State Balance. Stocks of phosphorite-glauconite ore and P_2O_5 are announced as having an uncertain industrial value by the State Service for Geology and the Subsoil of Ukraine (Table 2).

4. UTILIZATION OF PHOSPHORITES IN AGRICULTURE

According to the state Institution “Soil Protection Institute of Ukraine” [31], in 2018 189,200 tons of phosphorus (23 kg/ha of sowing area) were ordered by the agricultural enterprises for summer-autumn agricultural work. Ukrainian deposits can only partly supply the necessary amount of phosphate fertilizers. According to the geological and economic estimation, the most potentially valuable for development are considered to be complex apatite ores of the gabbro-anorthosite formations of the Korosten pluton (Stremyhorod, Fedorivka etc.), the formation of ultramafic alkaline rocks and carbonatites (in Novopoltavka). The similar deposits are exploited in Russia, South Africa, Norway. Apatite concentrates are characterized by high content of P_2O_5, being ecologically clean, they are suitable for processing without significant technological changes at the existing chemical plants of Ukraine [16]. On the other hand, complex apatite deposits explored in Ukraine require a considerable investment in order to begin their development. An alternative way can be the development of numerous explored phosphorite deposits, the raw materials of which are of lower quality and may be used inside the country. Below is a brief overview of the possibilities to use such raw materials.

For example, the calculations done for Zhvan mixed type deposit (Vinnytsia oblast) show that the processing of 14–16% ore concentrate from the deposit into superphosphate is unprofitable. However, phosphorite flour from concentrate or even from unenriched ore can be used directly for acid Podillia soils and can be as efficient as superphosphate. This fact was confirmed by the research on such agricultural crops as sugar beet, potatoes, winter wheat, oats, buckwheat, corn, and others. The flour from Zhvan ore, except for phosphorites, contains 30–40% of glauconite rich in potassium, therefore, the fertilizer can contain both phosphorus and potassium. Glauconite also contributes to the intensive development of bacteria producing nitrogen and enriching soil with nitrogen. It is also calculated [28] that if that ore is used for the production of phosphorite flour, a high rate of return (more than 30%) and a short pay-back period (about 3 years) can be reached. At the same time, the capacity of the future plant is expected to be 150 thousand tons of phosphorite flour per year.

On the deposit, organizing a small experimental and industrial enterprise for the production of phosphorite and glauconite flour from the richest types of ores without their additional beneficiation is recommended. The fact is that during the exploration of the deposit, definite areas with relatively rich ores (6–9% P_2O_5) with the considerable thickness of the productive layer (1–1.5 m) in favorable conditions for extraction were discovered. Flour made of such ores has successfully proved itself in the fields. The development of the deposit can be done only by the adits, though [14,28].

The use of local phosphorites and their influence on the crops yield was studied by the Polissia branch of National Scientific Center “Institute for Soil Science and Agrochemistry Research named after O.N. Sokolovsky” [15]. The conclusions are the following:

- granular and nodule phosphorites are valuable phosphate-limestone natural agricultural ores, the use of which enables a considerable influence on the soil fertility, crop yield and quality of agricultural products. They are considered to be ecologically clean raw material used for the production of complex fertilizers;
- the use of phosphorites as phosphate fertilizers on Alfisols helps to stabilize the balance between acid and base in soil solution during crop

rotations (potato, barley, spring clover). Depending on the norm, their usage changes the soil solution by making it more basic by 0.3–0.6 points;

- a comparative evaluation of the basic agrochemical properties of granular and nodule phosphorites indicates that their impact on the soil bio-productivity in the crop rotation zone is more effective than the one done by usual phosphate fertilizers (superphosphate, ammophos);
- the highest potato yield is directly gained with the use of granular phosphorites with double norm of P_{120}. It helps to increase the harvest of spring barley by 82–95% according to all norms, and green mass of the clover by 4–10% according to absolute control, and by 9–16% and 6–12% according to the standard variant. The direct action of nodule phosphorites increases potato productivity by 42–67%. After nodule phosphorites usage, the yield of spring barley grows by 71–95% and the yield of the green mass of red clover rises by 5–9% according to the control and by 2–16% and 2–12% respectively according to the stardard variant;
- the use of phosphorites on the drainaged peat soils leads to increase in crop yield comparing with the non-fertilized variant: perennial grass – 33.4 t/ha, corn for green weight – 14.6 t/ha, fodder beet – 15.6 t/ha which is almost as efficient as the use of superphosphate [32];
- granular and nodule phosphorites do not cause an accumulation of heavy metals in the soil, and the amount of nitrates in agricultural products is within the limits of permitted concentration. Local phosphorites contributed to a decrease in the accumulation of radiocaesium in the green mass of perennial grasses by 1.57–1.63 times [15].

The experience of experimental and industrial development of granular phosphorite de- posit in Karpivka, Donetsk oblast, done by joint-stock company “Agrofos” may be useful while preparing for the development of granular phosphorite deposits in Podillia.

The deposit includes phosphorite-glauconite-quartz sand and sandstone of Cenomanian age with an average P_2O_5 ore content of 5.86%. The technology of ore beneficiation was elaborated by the Ukrainian state Institute of Mineral Reserves. The development of the deposit began in 1999 by Amvrosiivka Mineral Fertilizers Factory, and during 1999–2001, 20 thousand tons of ore was extracted and enriched, and 7 thousand tons of phosphorite-glauconite concentrate was obtained. The work of the beneficiation factory proved the necessity to improve the technology of raw material beneficiation (the planned parameters of the concentrate were not achieved). examining the concentrate revealed that its quality predominates over the granular superphosphate for all soil climatic zones on condition that it is introduced in relevant doses for the digestible P2O5. The necessity of fine grinding of the phosphate product was not confirmed, therefore, agricultural enterprises successfully used phosphorite-glauconite concentrate in its natural form (0.25 mm) [12].

On the other hand, the state does not provide orders for phosphate fertilizers therefore their sales had to be done by direct contracts with agricultural consumers. However it was complicated in those conditions because the customers usually did not have cash. These and some other circumstances caused difficulties in selling products. The factory found the solution in improving the quality of the concentrate by means of the formation of composite mixtures with richer nodule phosphorites, further improvement of the technology of ore beneficiation, increasing the factory capacity which would lead to lowering the selling price and finally, advertising the products (agrofoska) on the internal market. An important condition for the efficient functioning of such mining enterprises is the conclusion of future contracts for the product supply to consumers [12].

Evaluation of phosphorite ores for chemical processing can consider the following possibilities [33]:

a) joint processing of apatite and low quality phosphorite raw materials in order to obtain average indicators;
b) beneficiation of phosphorite ores in order to produce phosphorite concentrates for further standard chemical processing;
c) application of innovative technologies of beneficiation and chemical processing of phosphorite raw materials to define certain conditions of raw materials.

Actually, the second direction of technological evaluation with obtaining phosphorite concentrate for chemical processing appears the most efficient in the short term. Granular phosphorites turn out to have the best prospects for standard processing among the traditional and new geological and industrial types of phosphorite ores.

The analysis of the use of traditional phosphate mineral fertilizers shows, however, that their efficiency is low due to the fact that plants consume only small amount of phosphorus, but acidic technology requires the maximum high content of P_2O_5 using only rich ores and high-quality reagents. In order to solve these problems, according to [34], implementing the method of the phosphorus mineral fertilizers production (containing calcium, magnesium and silicon), which excludes the use of sulfuric acid and implies the formation of gypsum as a waste product from phosphorus renovation by heating it to the temperatures of 800–1200° C directly from phosphorite ores is proposed. The complex processing of phosphorus raw materials appears to be highly environmentally effective and industrially productive with phosphates that are insoluble in water as its result. This approach enables the industrial development of numerous small phosphorite deposits with small initial capital and thus attracting a larger circle of investors to be started [34].

Chalk-phosphorite limestones, studied at the exploration stage in Khmelnytskyi and Vinnytsa Podnistrovia, in particular in Murovani Kurylivtsi and Mohyliv-Podilskyi districts, can be considered as powerful complex ameliorants. The content of P_2O_5 ranges from 2 to 5%, and the content of $CaCO_3$ is 76–85%. such ores do not require enrichment or chemical processing, since a mixture of two essential components, phosphorite and limestone flour, required for the vast majority of local soils are produced during grinding process. The phosphorite component of such flour is marked by a very high solubility degree as the content of the citrate-soluble form of P_2O_5 is more than 55–60% which is 1.5–2 times higher than in phosphorites imported to Ukraine from the Russian Federation which used to import the flour to Ukraine. Limestone component also works more efficiently than the one from dense limestone flour which is produced in the Vinnytsia oblast. The balance between the content of P_2O_5 and $CaCO_3$ in chalk limestones varies according to the local soil needs in these components [14,28].

Field studies of the sugar Beet Institute of the National Academy of Agricultural sciences of Ukraine confirmed [17], that phosphorite-chalk flour, obtained by grinding phosphate chalk limestone from one of Vinnytsia deposits, has the same efficient effect on the sugar beet yields and sugar content while being applied once as the total use of artificial phosphorus fertilizers (superphosphate or ammophos and traditional ameliorants such as limestone flour). The tests were carried out on typical Vinnytsia soils such as greyzems (sierozems) and chernozems.

The research also proves the chalk-phosphate flour to be efficient to be used for field beets, winter wheat, barley, rye, potatoes, perennial grasses. Practically all experiments that studied aspects of product quality indicate their improvement, sometimes quite a significant one. For example, the content of starch and vitamin C in potatoes grown using such flour is higher by 22 and 20%, respectively, and the content of nitrates is 1.5 times lower than in the potatoes grown using superphosphate.

The processing chalk rocks into flour is less work- and energy-consuming than dealing with significantly stronger limestones. The cost price per ton of phosphorite-chalk flour ranges from USD 2–3 to USD 5–7 [28] depending on the conditions of raw materials extraction. The cost of 1 ton of phosphorite flour containing P_2O_5 of 30% reaches USD 200 in Ukraine now.

The process of production and use of phosphorite-chalk flour is quite environmentally-friendly, because it does not involve the chemical or thermal processing of raw materials. Phosphorite flour, unlike chemical fertilizers, is practically unwashable from the soil and does not pollute the environment. The European Union and the Russian Federation have the experience of using this type of flour. Defining the area of phosphate-carbonate ores of the Upper Cenomanian and their P_2O_5 content requires further systematic research, especially in potential areas of Mohyliv Podnistrovia [20,14].

5. CONCLUSIONS

1. The chemical plants of Ukraine which specialize in the production of phosphate fertilizers use exclusively imported phosphorite raw materials, mainly from the countries of North Africa and the Middle east. Meanwhile, 7 deposits of complex apatite ores and 9 deposits of phosphorite ores have been explored, listed in the state Balance and prepared for

experimental and industrial exploitation. Currently, only one phosphorite deposit is being developed to a small extent, other deposits are not mined.

2. Apatite ores are represented by bedrock apatite, apatite-ilmenite, rare-metal-apatite, crust of weathering of serpentinite deposits; phosphorite ores are: nodular, granular phosphorites, phosphorite-glauconite and phosphorite-iron ores. At the same time, the total resources of industrial categories only constitute more than 71 million tons of apatite and more than 11 million tons of phosphorite ores calculated at 100% of P_2O_5. The given figures prove the ability to supply raw material to Ukrainian chemical plants to their full productive capacity for 57 years and enable, at least partially, to reduce the amount of expensive imports of phosphorite raw materials.
3. The ore of Ukrainian apatite-containing deposits is characterized by a relatively low content of the useful component and requires special beneficiation methods. Thoroughly explored apatite-containing bedrock gabbro-anorthosite deposits of Korosten pluton (Stremyhorod, Fedorivka, Nosachiv deposits, as well as carbonatite ores of Novopoltavka deposit) can be primarily recommended for exploitation. All those deposits are com- plex, therefore they require the construction of enrichment plants, focused primarily on the production of ilmenite or rare earths concentrate, apatite concentrates are considered to be a supplementary useful component. The investors for the exploration have been found, however, this expensive procedure and it is currently being slowed down due to unfavorable investment conditions in the country.
4. The alternative to the use of expensive apatite concentrates may be deposits of local phosphorites with low content of P_2O_5, explored on Volyn Podillia plate and Dnieper-Donets Rift (Zhvan, Myliatyn, Mateiky, Ratne, Osykove, Karpivka and other deposits). With the content of phosphorus up to 30%, they can be used directly as fertilizers. soluble forms of phosphate fertilizers are produced from highly concentrated phosphorite flour. Phosphorite fertilizer can be used to change the soil where the most sensitive to fertilizers plants (berry bushes, perennial grass, sugar beet, potatoes, etc.) grow. Other crops use its post-effect which makes it possible to quickly reach the appropriate level of soil phosphorus. Soil phosphorization is equivalent by its efficiency to other methods of applying phosphate fertilizers. More over, so-called granular phosphorite ores of Ukraine are considered to have various agricultural effect as a result of the connection with glauconite, carbonates and microelements and are considered to be the most ecologically-friendly fertilizers in the world due to their reduction of the content of nitrates in soils, etc. They have already started to be developed in Volyn and should form the main phosphorus raw material base for Ukrainian chemical enterprises. Further studies are required to accurately assess the quality of ores and reserves of phosphate-carbonate ores of the Upper Cenomanian of Mohyliv Podnistrovia, granular phosphorites of Volyn-Podillia basin, phosphorite deposits within Kryva Luka trough and others.
5. Phosphate carbonate ores (phosphate chalk) of Upper Cenomanian of Mohyliv Podnistrovia needs further studies in order to properly estimate

the quality of ores and reserves, as the ores can be used without expensive processing and be produced into phosphate chalk flour while grinding, which significantly increases the yield of a variety of crops according to previous research.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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This chapter is an extended version of the article published by the same author(s) in the following journal.
Gospodarka Surowcami Mineralnymi – Mineral Resources Management, 35(4): 5–26, 2019.
DOI: 10.24425/gsm.2019.128543