Phosphorites and Glaucnites as Additional Reserves in the Development of Titanium-Zirconium Sands of the Centralnoye Deposit (Tambov Region of Russia)

A F Georgievskiy¹, V M Bugina¹

¹Peoples’ Friendship University of Russia (RUDN University), Moscow, Russia

E-mail: georgievskiy-af@rudn.ru

Abstract. After the Soviet Union demise, Russia was plagued by severe titanium resource problems. The bulk of titanium concentrates is imported from Ukraine. But Russia has its own titanium resources not lesser than in leading countries of the world (China, Brazil, South Africa). Ores form both primary and alluvial deposits, including those located in economically developed regions. The better example is the ancient marine placer of the Centralnoye deposit in the Rasskazovsky district of the Tambov region. In addition to ilmenite, rutile and zircon, ore sands also include phosphates and glauconite. The deposit was discovered in the middle of the last century and, after geological prospecting, was classified as one of the ten largest world objects of placer titanium ores. Despite this, for many years the Centralnoye deposit remained abandoned, since by that time, in the Soviet Union in Ukraine, several mining plants were already operating, which satisfied the industry's demand for titanium. Today Russia is in dire need of titanium raw materials and the question of the need to develop the deposit has been repeatedly raised. This topic is being discussed especially actively today since a decision has been made on the expediency of its development. However, in the modern market environment, the implementation of this decision is an extremely difficult task. Here, the factors that can reduce operating costs that can improve the economic performance of mining and processing of ore sands become important. These factors include mining and use of both phosphorites and glauconites contained in titanium-zirconium ores and in the "overburden" rocks. The article describes the technogenic waste (tailings) of titanium-zirconium ores. Their material, mineral and granulometric composition is considered, and the technological properties of phosphorites and glauconites are described in the article. On the basis of experimental data, it has been shown that the accumulated concentrates represent high-quality raw materials for the production of phosphate rock and effective phosphorus and potassium ameliorants.

1. Introduction
The Centralnoye deposit is localized from 2 to 20 m from the surface among horizontally lying Upper Cretaceous sands. Phosphorites and glauconites are associated components of titanium-zirconium ores and form two contiguous horizons separated by an erosion surface. The lower Cenomanian horizon is confined to the top of the ore bed. The upper Santonian horizon, which directly overlaps it, together with the Quaternary deposits, belongs to overburden rocks. The average capacity of each of them is equal to one meter. In both cases, glauconites and phosphorites are represented by grains and nodules scattered in the sands [1,2,3,4,5,6,7]. The total reserves of phosphorites are estimated in the C₂
category and amount to 17 million tons of phosphorite concentrate with an average content of 14.3% \( \text{P}_2\text{O}_5 \). Approximate reserves of glauconite concentrate are estimated at 6 million tons [8,9,10]. The aim of the work was to show the possibilities of enrichment and practical use of glauconite and phosphorite products, incidentally, mined during the development of titanium-zirconium ores of the Centralnoye deposit.

2. Materials and methods
The materials for research were the data of studying two technological samples weighing 300 kg each. One of them (No. 51; 3.7% \( \text{P}_2\text{O}_5 \)) characterizes the upper, and the second (No. 53; 0.98% \( \text{P}_2\text{O}_5 \)) lower phosphorite-bearing horizons. The study of sample No. 53 was carried out on technological products remaining in the tailings of titanium-zirconium sands after their enrichment. To study the samples, a granulometric sieving of the material was carried out, followed by its separation by centrifugal analysis into its component parts. The obtained fractions were examined by conventional and electron microscopy, X-ray, chemical and quantitative spectral analyzes. For these purposes, the following devices were used: an optical microscope POLAM L213M, a stereoscopic microscope C13, a DRON-4 diffractometer, a LIES spectrometer, an EMV-100AK electron microscope, a SIM-1 separator, a GISL-62A mechanical screen, an MShR ball mill, a KSN-1.5 classifier, magnetic separator type 6ERM-35/315, hydrocyclone type GC-500. The analyzes were carried out in the laboratories of the State Institute of mining and chemical raw materials, RUDN University, Russian State University for Geological Prospecting.

3. Results and discussion
The ores of both horizons are loose, light-colored quartz sands with characteristic mica lustre, dotty dissemination of glauconite, and scattered phosphorite concretions of various sizes. In general, the Santonian sands, in contrast to the lower horizon, are thinner, with a significant admixture of a clay-zeolite substance (12.9%), glauconite (13%) and micaceous (7%). In addition, they contain more phosphorites (12%) of higher quality (22.4% \( \text{P}_2\text{O}_5 \)). The sands of the lower (Cenomanian) horizon are quartz (83%), depleted in phosphates (3%; 9-15% \( \text{P}_2\text{O}_5 \)), glauconite (4.6%) and micas, but enriched in heavy minerals (4%). The content of feldspars, as in the upper horizon, is 4%. Ores - sands consist of (80-90%) fine grades (-0.25 mm). Most of the phosphate formations are associated with large classes (> 2 mm), where 60-70% of the recoverable \( \text{P}_2\text{O}_5 \) is concentrated. A noticeable amount of phosphates is also concentrated in the class -0.15 + 0.1 mm and -0.04 mm. However, the low content of the useful component (1-2% \( \text{P}_2\text{O}_5 \)) makes such classes not promising for practical purposes. Thus, at the Centralnoye deposit, phosphate is observed in the form of dominant large lumps and subordinate psammitic grains. Coarse phosphorite material consists of authigenic and reworked nodules, small pebbles, and organic remains. Authigenic nodules are characteristic for the phosphorite of Santonian horizon, and various reworked material is characteristic for Cenomanian level.

The total content of \( \text{P}_2\text{O}_5 \) in ores is determined by phosphorite nodules. Their morphology is different, but isometric contractions 5-8 cm in size predominate. The larger ones have a bizarre configuration with characteristic protrusions and outgrowths. Smaller nodules - with traces of rolling. They are usually covered with a yellowish-gray coating of powdered phosphate, often masking the natural brown color. Macroscopically, the nodules are rough, strong, dense, and consist of small nodules that have been repeatedly cemented with phosphate of recent generations. The latter on the cleavage and in thin sections are established by alternating dark and light areas with different structural and textural features. Inside the nodules, there are casts of small pelecypods, and on the surface there are holes from stone borers mollusks. Also, not uncommon are the winding passages of burrowing mud-eaters organisms filled with fine-grained sand. Some of the passages along the walls are inlaid with needle-shaped zeolite crystals. Some concretions (10-15%), especially washed out from the Cenomanian deposits, are weathered. They are white in color, have an earthy fracture, and disintegrate easily.
In thin sections, nodules are composed of isotropic phosphate, which cements glauconite-quartz material. The latter is concentrated in spots, stripes, scattered inclusions. Sometimes they are surrounded by crystallized thin phosphate rims. In general, the basal type of cement is characteristic with a stable predominance of phosphate over terrigenous quartz, so that the amount of P2O5 in the concretions reaches 20-25%. This significantly distinguishes the Santonian formations from the Cenomanian phosphorites, often of low quality, with a mass fraction of P2O5 equal to 9-15%.

Other impurities in phosphorites include glauconite (1-5%), feldspar (1-2%), and rare grains of heavy minerals. Fragments of microquartzites, nests of clay matter, and organic remains are also noted. The latter are developed insignificantly, but after phosphate accumulations, they form the second morphological type of phosphate segregations in the ores of the Centralnoye deposit. There are macro- and micro-remains. The first ones accumulate in the + 7 mm class. Among them, gastropods and pelecypods casts, fragments of phosphatized sponges occur. Sometimes, entire sponges 15-20 cm in size are preserved.

Phosphate micro-residues are represented by coprolites, pseudomorphs after foraminifera, radiolarians, and sponge spicules; fragments of fish bones are also found. Unlike large classes, where the remains of organisms are of no practical importance, in the sands they account for the bulk of phosphates. The most common coprolites are 0.04-0.25 mm in size. The coprolites are spherical, lenticular, or in the form of shortened sticks. The color is different: from black and blue to white and yellow; the surface is matte, smooth, or rough; many of them have a glassy appearance. Coprolites are composed of isotropic phosphate, often recrystallized to apatite. Thus, 4 modifications of phosphate are established: isotropic cryptocrystalline, crystalline radial-radiant, crystalline apatite-like, isotropic powdery of supergenic nature. Isotropic phosphate composes most of all phosphate formations. Average refractive index 1.559-1.605; density 2.85 g/cm³. Radial-radiant phosphate forms rims (0.01-0.02 mm) around various irregularities in phosphorite nodules. The refractive index of the mineral is 1.603-1.605; birefringence -0.005-0.007; density 2.85 g/cm³. Other parameters of the two noted differences of phosphate: "a" = 9.323-9.334 Å; "C" = 6.899-6.896 Å; CO2 / P2O5 = 0.155-0.176; F / P2O5 = 0.094-0.11; P2O5 content in the enriched fractions - 29.2 - 32.35%. According to the data [11, 12, 13, 14, 15], the given indicators are typical for the Kurskite mineral. Isotropic powdery phosphate forms tarnish on nodules and is also noted among the pelritic material of the -0.04 mm class.

The dispersed sizes of particles, their intergrowth with other minerals do not allow correct measurements of the refractive index and determine the X-ray structural parameters of the substance. However, the phosphate nature of the particles is proved by the reaction with a solution of ammonium molybdate. Apatite-like phosphate is the last known modification of the phosphate mineral in ores. It is quite widely represented in sands in a fraction of density 2.8-3.0 g/cm³, where it composes grains of sand, coprolites and other small organic remains. In immersion solutions, transitions are observed from phosphate grains, isotropic and partially recrystallized, to converted into single crystals of apatite, completely extinguished with the rotation of the microscope stage. At the same time, the phosphate particles become translucent, and their color changes to light blue and blue. Along with apatite grains, plates and crystals of violet fluorite were found. This mineral association indicates recrystallization of isotropic phosphate to fluorapatite, accompanied by a partial loss of fluorine. The latter, after minor migration, crystallized in the form of fluorite. The data of crystalloptic and X-ray structural analyzes confirm the apatite nature of the mineral. Its refractive index is 1.623-1.627; unit cell parameters: "a" = 9.349-9.37 Å; "C" = 6.868-6.896 Å. In [12, 16] it is shown that the transition of kruskite to fluorapatite is achieved during deep catagenesis and metamorphism.

The geological position of the Centralnoye deposit, the poorly lithified (loose) consistency of the sands containing phosphorites, does not allow us to associate the recrystallization of kruskite with catagenesis. Obviously, there are other factors causing the transformation of phosphate minerals. It can be assumed that ancient supergenic solutions have an aggressive effect on the sands, traces of which are recorded in the ores in the form of weathered phosphorite formations, altered feldspars and micas. Probably, under the influence of such solutions, part of the phosphate substance was redeposited in the form of tarnishes of powdered phosphate. The other part underwent a structural transformation with a
transition to apatite. The ability of supergene solutions to change the structure of phosphate minerals is shown in many papers [17, 18].

3.1. Technological properties of phosphorites

The enrichment of ores depends on their physical, material, structural-textual and mineralogical-petrographic features [12,13,14]. The phosphorite ores of the Centralnoye deposit are represented by loose sands with scattered dense phosphorite formations. As shown by granulometric studies and the distribution of phosphorus pentoxide by fractions, phosphate-rich material is concentrated in large grades. These features of the ores make it effective as a first technological operation to screen out fine grades of phosphates. The analysis of possible screening options showed that the optimal screening of ore is + 0.5 mm for the upper, and + 2.0 - for the lower phosphorite horizons. These options maximally satisfy in terms of the completeness of the extraction of phosphates, while maintaining the quality of concentrates at the level of products applicable in the national economy.

When organizing screening on an industrial scale, an important practical task is to assess the manufacturability of screening without involving ore washing. For this purpose, experiments were carried out on the sieve of ores of the upper horizon by "dry" and "wet" methods. With dry sieving, there is a sharp drop in the quality of the concentrate and other beneficiation parameters. The reasons lie in the high content of dispersed clay and zeolite minerals in the sample. Their presence on the surface of the phosphorite material leads to a "coarsening" of the granulometric composition and sharp contamination of the screened-out concentrates with non-phosphate impurities. Thus, ore washing is a prerequisite for the concentration of phosphorites from the Centralnoye deposit. Washed phosphorite concentrates consist of nodules and sandstone fragments, the amount of which is estimated from 21% (sample 51) to 30% (sample 53). Taking into account the significant difference in the strength properties of phosphorites and sandstones, for further enrichment of concentrates, experiments were carried out on selective destruction of sandstones under conditions of autogenous grinding of ore, followed by screening out of its fine classes. Thirty-minute ore rolling leads to the destruction of sandstones, as a result of which in concentrates, after screening out of small classes, the content of phosphorus pentoxide increases by 3%. However, the positive effect of such a technological operation is offset by losses in the extraction of phosphate, which reach 51%.

To obtain phosphate products suitable for the production of soluble fertilizers, it is required to purify concentrates from diluting impurities trapped inside phosphorite nodules. This can be achieved only after their destruction and the disclosure of non-phosphate minerals. Here, the fineness of the crushing of the concentrate and the ability of the noted minerals to separate in independent grains are of paramount technological importance. According to the study of thin sections, the minimum number of intergrowths will be formed at a grinding fineness of -0.1 mm, which is determined by the size of mineral inclusions in nodules. The degree of opening of minerals and the ability of phosphorites for deep enrichment are assessed by the gravitational separation of crushed material when centrifuged in heavy liquids. Experiments have shown that phosphate is present in all fractions, but the richest material in it is material with a density of -3.0 +2.85 g / cm3 (23-25% P2O5). However, even here it is not possible to achieve satisfactory purification of phosphate, since it is 25-30% contaminated with foreign impurities in the form of phosphate intergrowths with glauconite and quartz. At the same time, the studies carried out show that it is possible to obtain high-quality phosphate products at the level of 28-29% P2O5, but for this, the content of phosphorus pentoxide in the feedstock must be at least 21-22%. When focusing on such raw materials, only 50% of the recoverable phosphates of the upper phosphorite horizon alone will be involved in processing, and therefore the practical implementation of this option is unlikely. In this regard, it is important to assess the possibility of using the washed phosphorite concentrates themselves in the national economy.

Evaluation of the practical suitability of phosphorites. Since the phosphorite concentrates of the Centralnoye deposit are not suitable for obtaining soluble fertilizers, it is advisable to study the possibility of their use as phosphate powder. As you know, on acidic soils, such fertilizer competes in efficiency with superphosphate. Taking this into account, experiments were carried out to obtain...
phosphate powder of ordinary (0.18 mm) and fine (0.1 mm) grinding. The research was carried out using a Roalgang-type ball mill. As can be seen from the table, standard and fine ground phosphate powder from the Centralnoye deposit is not inferior to the concentrates of the developed Verkhnekamskoe deposit in terms of the $P_2O_5$ content (LR) (Table 1). Hence, it can be used as a mineral fertilizer.

| deposit                  | phosphate powder type | content, % | $P_2O_5$ (general) | $P_2O_5$ (soluble in citric acid) |
|--------------------------|-----------------------|------------|--------------------|-----------------------------------|
| Centralnoye, sample 51   | standart              | 20.13      | 7.3                |
|                          | fine                  | 20.13      | 7.5                |
| sample 53                | standart              | 14.3       | 6.95               |
|                          | fine                  | 14.3       | 7.1                |
| Verkhnekamskoe [12]      | standart              | 22.5       | 6.2                |
|                          | fine                  | 22.5       | 6.5                |

3.2. Characteristics of glauconite

Glauconite is observed in all granulometric classes in the form of various grains, pseudomorphs and microconcretions 0.01-0.5 mm in size, more often 0.07-0.15 mm in diameter. Two generations are established, differing in density properties, magnetic susceptibility, and morphogenetic characteristics. Glauconite with a density of 2.75-2.85 g / cm3 is concentrated in the ores of the lower horizon. It is represented by rounded isometric grains and their fragments of dark green, almost black color, with a glossy surface. In thin sections the grains are brownish-green with a pronounced microaggregate extinction. Mineral accumulates on the electromagnetic separator at a current of 0.2 Å. According to the ratio of Fe and Al, it belongs to the ferrous variety ($Fe_2O_3 / Al_2O_3 = 2.1$).

According to the results of X-ray structural studies, it is a high-iron hydromica of the 1M polytype, containing 5% montmorillonite packages. Glauconite with a density of 2.6-2.75 g / cm3 is typical for the upper phosphorite-bearing horizon. It is most often observed in the form of light-colored microconcretions and pseudomorphs after mica scales. Microconcretions have an irregularly isometric shape, a bunch-like structure. In thin sections, it is characterized by a “palmate” configuration and distinct aggregate polarization. When interacting with electromagnetic fields, the mineral is separated at a current strength of 0.3-0.4 Å. According to the ratio of Fe and Al oxides, it is considered as a low-iron variety of glauconite ($Fe_2O_3 / Al_2O_3 = 0.8$). According to X-ray structural analysis, it is a mixed-layer mica-montmorillonite formation with an ordered structure of the 1M polytype, with 25-30% of swelling layers. In order to find out the maximum possible indicators of separation on products with a removed clay component, experiments were carried out to separate glauconite from "sands" using a high-performance separator "Boxmag-Rapid" (England). The results obtained show that the isolated magnetic fractions are almost entirely composed of glauconite. From the “sands” poor in glauconite, sample No. 51, only 20-27% of glauconite pass into the magnetic fraction. On the contrary, for sample no. 53, with an increased mineral content, this parameter does not fall below 80%. Thus, the "sands" of the upper horizon are promising for obtaining high-quality glauconite concentrates, while the "tailings" from washing the ore sands of the lower horizon are of little use for these purposes.

3.3. Results of agrochemical evaluation of phosphorite powder of the upper and potassium glauconite-phosphorus ameliorant of the lower horizons

Studies of agrochemical properties were carried out during vegetation experiments with oats on acidic (pH-4) gray forest soil with a low content of mobile phosphorus (2.5 mg $P_2O_5$ per 100 g of soil). These products were used as fertilizers in powder form with a particle size of -0.18 mm. The results obtained indicate that under the influence of the products introduced into the soil, there was a noticeable improvement in the conditions of phosphate-potassium nutrition of oats and an intensive growth of the vegetative mass of plants (25% sample no. 51; 26% sample no. 53).
4. Conclusions
To clarify the possibility of waste-free mining of the Centralnoye deposit, the material composition, washability and ways of using phosphorites and glauconites of technological samples No. 51 and 53, characterizing natural and technogenic ores of loose sands of the upper and lower phosphorite horizons, were studied. The ore of the upper horizon, in contrast to the lower one, is characterized by an increased amount of coarse material, a thinner silty-pelitic composition of the sandy groundmass, an abundant admixture of clay-zeolite matter, a reduced content of "heavy" minerals, an increased proportion of glauconite and better quality of phosphorites. The bulk of phosphorites accumulates among lumpy material in the form of nodular concretions, which are considered to be nodular phosphorites. The other, predominant part of phosphates is confined to sandy granulometric classes, where they are observed in the form of phosphatized grains of coprolite nature. "Sands" are multicomponent and along with the noted minerals include zeolites, montmorillonite, muscovite, feldspars.

The content of phosphorus pentoxide in concentrates depends on the amount of sandstone fragments present in their composition and on the quality of the nodules. These two indicators explain the sharp qualitative differences between the ore concentrates of the lower (13% P₂O₅) difference and the upper (18-20% P₂O₅) horizons. There is a fundamental possibility of improving the parameters of concentrates due to the destruction of sandstones in the course of technological "rolling" of the material. However, the results obtained from these operations are reduced to naught due to significant losses in the extraction of P₂O₅. According to the main parameters, the concentrates under consideration can be used as phosphoric fertilizers in the form of phosphate rock (sample no. 51) and its low-quality substitutes- phosphomeliorants (sample no. 53). The carried out vegetative experiments have proved the high agrochemical capabilities of finely ground and ordinary phosphate powder, as well as phosphomeliorants.

Obtaining glauconites from the tailings is possible by electromagnetic separation after screening out dust-like fractions. As a result of beneficitation, two concentrates with 87% and 62% glauconite were isolated, which characterize the "sands" of the upper and lower horizons, respectively. In both cases, the recovery of the mineral is low. Although, as shown by laboratory experiments, there are reserves for improving the enrichment indicators. It is ineffective to enrich the "lower" "sands". From many existing directions of using glauconite, the possibilities of using the obtained glauconite concentrates as a chlorine-free potassium fertilizer have been analyzed. The performed vegetation tests have shown the high efficiency of concentrates as such fertilizer.

5. References
[1] Ikonnikov N N 1987 Productive placer formations of the sedimentary cover of the Russian platform 8th meeting on the geology of placers (Kiev) IGFM AN SSSR pp 249–250
[2] Savko A D, Belyaev V I, Ikonnikov N N, Ivanov D A 1995 Titanium-zirconium placer of the Centralnoye Black Earth Region (Voronezh Voronezh State University) p 147 https://elibrary.ru/item.asp?id=21067578
[3] Laverova N P, Patyk N G 1997 Placer Deposits in Russia and Other CIS Countries Ed Moscow Scientific world p 454 https://www.geokniga.org/books/5337
[4] Patyk-Nara N G, Gorelikova N V, Bardeeva E G 2004 On the history of the formation of titanium-zirconium sands of the Centralnoye deposit in the European part of Russia Lithology and useful minerals 6 pp 585-601 https://elibrary.ru/item.asp?id=17657530
[5] Patyk-Kara N G, Levchenko E N, Stekhin A I, Barsegyan V V, Bochneva A A, Chizhova I A, Andrianova E A, Dubinchuk V T 2008 Mineral associations of titanium-zirconium sands of the Centralnoyedeposit (East European platform) Geology of ore deposits 2008 3 pp 246–270 https://elibrary.ru/item.asp?id=10209414
[6] Lalomov A V, Remizova L I 2015 Main directions of creation of import-independent titanium and zircon mineral resource industry of Russia (RKV-2015) (Perm) Perm State National Research University pp 129–131 https://elibrary.ru/item.asp?id=25224259
[7] Savko A D, Dmitriev D A, Kurolap S A et al 2018 Fundamentals of optimal use of the mineral resource base of the Centralnoye Black Earth region (Voronezh: Voronezh State University) p 92 https://elibrary.ru/item.asp?id=36970251

[8] Information on the state and prospects of using the mineral resource base of the Tambov region as of 01.01.2018 (St. Petersburg: FSBI "VSEGEI" http://atlaspacket.vsegei.ru/#a3a66ba22abcf09510 (tested on 16.12.2019)

[9] State report On the state and use of mineral resources of the Russian Federation in 2016–2017 (Moscow: FGBU VIMS) Mineral-Info p 370 https://www.mnr.gov.ru/docs/o_sostoyanii_i_ispolzovanii_mineralno_syrevykh_resursov_rossiyskoy_federatsii/2017_doklad_o_sostoyanii_i_ispolzovanii_mineralno_syrevykh_resursov_rossiyskoy_federatsii/

[10] Lalomov A V, Bochneva A A 2020 Central, Lukoyanovskoe and Unechskoe deposits of zirconium-titanium sands as a basis for creating a mineral resource center and implementing a strategy for import substitution of Russia Young Scientist 2 pp 333-341 URL: https://moluch.ru/archive/292/66268/

[11] Bushinsky G I 1954 Lithology of Cretaceous deposits of the Dnieper-Donetsk depression Moscow Publishing house of the Academy of Sciences of the USSR p 307 https://search.rsl.ru/ru/record/01005765166

[12] Bliskovsky V Z 1983 Material composition and concentration of phosphorite ores Moscow Publishing house Nedra p 199 https://search.rsl.ru/ru/record/01001173703

[13] Smirnov A I 1972 Material composition and conditions for the formation of the main types of phosphorites Moscow Publishing house Nedra p 194 https://search.rsl.ru/ru/record/01007448599

[14] Bliskovsky V Z, Mineev L A 1986 Fertility stones Moscow Publishing house Nedra p 213 https://search.rsl.ru/ru/record/01001330484

[15] Sokolov A S 1991 The main problems of phosphate geology Problems of the geology of phosphorites (Moscow: Publishing house Science) pp 184 https://search.rsl.ru/ru/record/01001587256

[16] Krasilnikova N A 1963 About fluorite in phosphorites Lithology and mineral ressources 3 pp 141-144

[17] Bugina V M, Yudovich Ya E, Ketris M P 2016 Lithochemical characteristics of karst phosphorites of Haranurskoe deposit (South-Eastern Sayans) Bulletin of the Institute of Geology of the Komi Russian Academy of Sciences 8 pp 33-37

[18] Georgievskiy A F 2004 Karst phosphorites of the Southeastern Sayan Mountains Modern engineering technologies (Moscow, RUDN) pp 65-67