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# RESOURCE POTENTIAL OF CHEMICAL AND AGROCHEMICAL MINERAL RAW MATERIALS IN UKRAINE

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#### INTRODUCTION

Mining and chemical raw materials are divided into chemical, agrochemical and mineral pigments. The first includes minerals and rocks that are widely used in the chemical industry – rock, potassium and magnesium salts, bischofite, sulfur, iodine, bromine, etc. Mineral pigments (mineral paints) are rocks or minerals that do not dissolve and do not lose color in water, various colored rocks and minerals in oil and alcohol, and together with varnish, oil, organic glue, liquid glass and other substances are the main

components of paints (ochre, malachite, sienna, mummy, glauconite, vivianite, etc.). Agrochemical raw materials include a number of minerals and rocks that, for one reason or another, contribute to increasing soil fertility and stimulate the productivity of agricultural production. We present the proposed division of agrochemical raw materials by purpose in the table 1. As can be seen from the table, many types of mineral agrochemical raw materials have a wide range of applications in crop and animal husbandry. The problem, however, is that in the conditions when large collective farms have actually ceased to function, and the processes of establishing strong farms are unduly stretched over time, many types of agrochemical raw materials are not used, which causes the conservation of many explored promising deposits of bentonites, glauconites, limestones, dolomites, etc.

# 1. Carbonate mining and chemical raw materials as an object of research in Ukraine

In Ukraine, quite significant deposits of valuable agrochemical raw materials (apatites, phosphorites, saponites, rock and potassium salts, sulfur, slag, ash, glauconite, chalk, limestones, etc.) have been discovered, which are currently being developed in limited quantities, or not at all. are developed at all, despite the acute shortage of such raw materials in the state.

The National Program for the development of the mineral and raw materials industry until 2030 provides for the urgent creation of own production of scarce types of mineral raw materials imported from other countries and without which the work of existing domestic metallurgical, chemical and other enterprises is impossible 1. Ukrainian chemical plants that specialize in the production of mineral fertilizers (Vinnytsia Chemical Plant, VAO «Sumikhimprom», CJSC «Dniprovskyi Zavod Mineralnyh Dobrivy») work on imported raw materials. At the same time, in agriculture, the shortage of fertilizers (primarily phosphorus) causes not only a drop in yield, but also soil degradation, which has already begun.

In the last decade, extensive exploration and evaluation work carried out by the DRGE «Pivnichgeologiya» aimed at determining the prospects of the Volyn-Podilsky region with regard to the detection of industrial concentrations of various types of agrochemical raw materials, gave positive results. Deposits of mineral raw materials unique to Ukraine – saponites, as well as granular phosphorites, glauconites, and apatites – have been established and pre-estimated, which makes it possible to revise established views

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<sup>&</sup>lt;sup>1</sup> Закон України: Про затвердження Загальнодержавної програми розвитку мінерально-сировинної бази України на період до 2030 року. *Відомості Верховної Ради України*. 2011. № 44. ст. 457.

Table 1

Classification of agrochemical raw materials<sup>2</sup>

|     | Classification of agrochemical raw materials |  |  |  |  |  |  |
|-----|--|--|--|--|--|--|--|
| №   | Types of agrochemical raw materials          | Use in agriculture                             |  |  |  |  |  |
| 1   | Phosphorite, apatite, kainite,               | Ores are carriers of basic (phosphorus,        |  |  |  |  |  |
|     | sylvinite, carnalite, sulfur, etc.           | potassium, nitrogen), secondary (magnesium,    |  |  |  |  |  |
|     |  | sulfur) chemical elements and trace elements   |  |  |  |  |  |
|     |  | (boron, copper, zinc, molybdenum,              |  |  |  |  |  |
|     |  | manganese, etc.), important for plant          |  |  |  |  |  |
|     |  | nutrition. They are used in the production of  |  |  |  |  |  |
|     |  | mineral fertilizers                            |  |  |  |  |  |
| 2   | Limestone, dolomite, chalk,                  | Ameliorating breeds used for chemical soil     |  |  |  |  |  |
|     | gypsum, saponite, glauconite,                | amelioration                                   |  |  |  |  |  |
|     | zeolites, ashes, granular                    |  |  |  |  |  |  |
|     | phosphorites                                 |  |  |  |  |  |  |
|     | Bentonite, palyhorskite;                     | To optimize the physical and chemical          |  |  |  |  |  |
| 3.2 | Zeolites, glauconite, vermiculite,           | properties of depleted soils, including for:   |  |  |  |  |  |
|     | palyhor-skite, diatomite, trepel;            | 3.1) structuring (structuring) of sandy soils; |  |  |  |  |  |
| 3.3 | Zeolites, bentonite, glauconite,             | 3.2) structuring and aeration of soils;        |  |  |  |  |  |
|     | palyhorskite, diatomite, trepel,             | 3.3) water retention, adsorption of pesticides |  |  |  |  |  |
|     | granular phosphorites;                       | and radionuclides from soils;                  |  |  |  |  |  |
| 3.4 | Glauconite, ashes, saponite                  | 3.4) soil reclamation                          |  |  |  |  |  |
| 4   | Rock salt, zeolites, bentonite,              | Mineral additives and feed fillers             |  |  |  |  |  |
|     | vermiculite, sapropel, saponite, etc.        |  |  |  |  |  |  |
| 5   | Talc, bentonite, zeolites,                   | Fillers of poisonous chemicals                 |  |  |  |  |  |
|     | palyhorskite, trepel, diatomite              |  |  |  |  |  |  |
| 6   | Zeolites, palyhorskite, vermiculite,         | Additives that prevent caking of mineral       |  |  |  |  |  |
|     | talc-magnesite, trepel                       | fertilizers                                    |  |  |  |  |  |
| 7   | Zeolites, peat, vermiculite                  | Hygienic bedding for livestock with            |  |  |  |  |  |
|     |  | subsequent use in the fields                   |  |  |  |  |  |
| 8   | Zeolites, glauconite                         | Stimulators of fish growth and for cleaning    |  |  |  |  |  |
|     |  | water bodies                                   |  |  |  |  |  |
| 9   | Glauconite                                   | To reduce the morbidity of industrial crops    |  |  |  |  |  |
| 10  | Zeolites, bentonite, palyhorskite,           | For the production of compound feed and        |  |  |  |  |  |
|     | syncyrite, diatomite                         | concentrates                                   |  |  |  |  |  |
| 11  | Zeolites, bentonite, glauconite,             | For sewage treatment and deodorization         |  |  |  |  |  |
|     | diatomite, trepel, saponite                  | (in animal husbandry)                          |  |  |  |  |  |

on the mineral resource potential of the region. At the same time, such a cheap type of agrochemical raw material as carbonate, whose application possibilities in agricultural production and the chemical industry are currently underestimated, remains out of the attention of exploration and processing

<sup>&</sup>lt;sup>2</sup> Сивий М. Я. Мінеральні ресурси Поділля: конструктивно-географічний аналіз і синтез: монографія. Тернопіль: Підручники і посібники, 2004. 656 с.

enterprises. Therefore, in this article we present a concise analysis of the main types of carbonate agrochemical and chemical raw materials of the country (raw material for liming acidic soils, feed additives, sugar industry, soda production), its real, reliable reserves, the current state of use and prospects, especially since other types of agrochemical raw materials have been considered by us in a number of previous publications<sup>3</sup>, <sup>4</sup>.

Analysis of recent publications on the research topic. Special studies of carbonate raw materials in Ukraine in the constructive and geographical aspect were not conducted. A regional analysis (Podillia) of this type of raw material is presented in the monograph of M. Syvy<sup>5</sup>. A general overview of the resource base of carbonate chemical and agrochemical raw materials in Ukraine is provided in the monograph by M. Syvy, I. Paranka, and E. Ivanov<sup>6</sup>, however, the data analyzed in these works require a critical review in connection with changes in the economic situation in the country and market conditions of carbonate raw materials.

# 2. Carbonate raw material for liming acidic soils and production of fodder supplements

For the needs of agriculture, mainly for liming acidic soils, limestone or dolomite flour is used, that is, the product of grinding limestones, dolomites, marly limestones, chalk and other rocks, which consist mainly of calcium carbonate and magnesium carbonate. Limestone flour must meet the requirements of DST 14050-78 «Limestone flour. Technical conditions», according to which the content of  $CaCO_3+MgCO_3$  in flour should be at least 86%. The moisture content of the flour should not exceed 4-6%. Impurities of quartz and clay reduce the quality of flour.

The optimal dose of flour application depends on the acidity and mechanical composition of the soil and ranges from 1,0–1,5 to 8–10 t/ha of  $CaCO_3$ . Lime liming of soils gives a significant yield increase, especially for those agricultural crops that are sensitive to high acidity. So, for moderately acidic soils, the yield allowance is: cereals – 2–4 t/ha, corn, sugar beet,

<sup>4</sup> Сивий М. Я. Фосфатні руди України як перспективні меліоранти. *Історія української географії*. Тернопіль, 2011. Вип. 22. С. 90–96.

<sup>5</sup> Сивий М. Я. Мінеральні ресурси Поділля: конструктивно-географічний аналіз і синтез: монографія. Тернопіль: Підручники і посібники, 2004. 656 с.

<sup>&</sup>lt;sup>3</sup> Syvyi M., Demyanchuk P., Havryshok B., Zablotsky B. Phosphates of Ukraine as raw materials for the production of mineral fertilizers and ameliorants. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management*. Warszawa, 2019. Volume 35. Issue 4. Pages 5–26.

 $<sup>^6</sup>$  Сивий М. Я., Паранько І. С., Іванов Є.В. Географія мінеральних ресурсів України. Монографія. Львів: Простір, 2013. 683 с.

carrots -30–40, cabbage -40–45, clover -8–10 t/ha. On highly acidic soils, the allowance is even higher.

The effect of soil liming manifests itself for quite a long time – more than 8-10 years. During this time, each ton of calcareous materials gives an additional crop (in terms of grain) of 1,2-1,5 tons. The cost of the additional crop exceeds the necessary costs by 10-15 times<sup>7</sup>.

Chalk is a traditional mineral additive for poultry. The calcium content in chalk ranges from 32,9 to 37,0%. It also contains phosphorus, potassium, sodium, magnesium, silicon, sulfur, iron, as well as harmful elements fluorine (0.01%), lead (0.006%), etc. When using chalk, you should be very careful, as there is a danger of mistakenly replacing the fodder mold with a construction one. Despite the complete external similarity, the presence of glue and cement, non-fodder products, is allowed in construction chalk, it contains an increased level of heavy metals and harmful substances. Such chalk becomes not a source of mineral substances, but the cause of acute fodder toxicosis in poultry. Turtles – empty shells of dead molluscs – are also used for mineral feeding of birds. In addition, their large particles perform the function of gravel in the stomach. Calcium content in shells depends on the fraction. So, the small fraction (1 mm and less) contains only 8,8% calcium, and 78,5% – impurities (sand, gravel, etc.), the medium (1,1-5.0 mm) – 31.8% calcium and in large (5.1 mm and more) – 33.3%. The calcium content in limestones depends on their origin and variety and is 33% on average. In addition to calcium, limestones contain iron, magnesium, sulfur and other trace elements<sup>8</sup>.

For use as a mineral supplement to the diet of farm animals and poultry, carbonate raw materials must comply with DST 21-37-78 «Chalk and limestone for mineral feeding of farm animals and poultry». Raw materials should not contain fluorine (more than 0,15%), arsenic (more than 0,012%), lead (more than 0,008%). The need to use mineral supplements in the diet of birds is connected, in particular, with the need for calcium, the lack of which leads to a decrease and cessation of egg laying, a decrease in quality, an increase in the number of eggs, etc. Limestone flour for mineral feeding of livestock must comply with MRTU 21-41-69 and contain at least 85% of CaCO<sub>3</sub>, not more than 5% of insoluble residues of P<sub>2</sub>O<sub>5</sub> or MgCO<sub>3</sub>, the content of toxic substances (F, As, Pb, Ba) is not allowed. Dolomite flour must comply with MRTU 1-65 and contain more than 85% calcium carbonate and

 $<sup>^{7}</sup>$  Блисковский В. З., Киперман Ю. А. Агрономические руды. М. : Знание, 1987. 48 с.

<sup>&</sup>lt;sup>8</sup> Мельник В. В. Вітамінні і мінеральні корми для птиці взимку. *Сільський двір.* Київ, 2013. № 1. С. 28–29.

magnesium in total, and up to 8% moisture. The quality of ground chalk is determined by DST 21-10-74<sup>9</sup>.

The resource base of carbonate raw materials of Ukraine is presented in Table 2.

Deposits of carbonate raw material suitable for liming acidic soils are explored within the boundaries of the Ukrainian Shield, the Volyn-Podilsky Plate, the Carpathian Folded Region and are mainly associated with layer-like deposits of the Neogene Sarmatian Regiolayer, less often – the Turonian Cretaceous layer. The thickness of the useful layer ranges from 3,5 to 26,0 m.

Limestone and chalk deposits, suitable for feed additives, are widespread within the Ukrainian shield, the Dnipro-Donetsk and Black Sea basins among the deposits of the Sarmatian and Pontic regio-layers of the Neogene, sometimes of the Cretaceous system and are represented by layer-like deposits of limestone or chalk with a thickness of 2,0–3,0 to 50,0–60,0 m. Rakusha is found as impurities in quartz-detrital sands distributed along the coast of the Sea of Azov.

Most of the explored deposits and reserves of carbonate agrochemical raw materials are concentrated in three regions of Podillia. One promising limestone deposit for liming acidic soils with significant reserves (Bilokorovytske) is located in Zhytomyr region. In total, in 2020, only 7 deposits were developed in Ukraine, from which 105,7 thousand tons of raw materials were extracted.

Precambrian crystalline limestones were discovered by quarries in the vicinity of the town of Lypovets, the city of Hnivan, in the villages of Vakhnivka, Sabarovo of the Vinnytsia region and are represented by lightgray, medium- and coarse-grained dense varieties, which are currently insufficiently studied and have no practical significance.

Limestones of the Silurian age lie shallowly in the southern regions of the Podilsky region and are used mainly as rubble and crushed stone raw materials in road and civil construction. Frequent dolomitization, chemically heterogeneous composition and the presence of a significant amount of impurities make them unsuitable for use in the sugar industry and not suitable for lime production (a high degree of recrystallization, which requires a significant increase in the firing temperature).

Carbonate rocks of the Cretaceous system are represented by deposits of the Cenomanian, Turonian, Coniacian and Santonian layers. Chalk deposits exposed in the valleys of the Dniester, Lyadova, Murafa, Nemia and other

<sup>&</sup>lt;sup>9</sup> Державний стандарт України «Крейда природна. Мука вапнякова». Терміни та визначення. ДСТУ БА -1.1-20-94. Київ: Держстандарт України, 1994. 4 с.

rivers are associated with the Cenomanian deposits in the Vinnytsia region. The possibility of using rocks by industry has not been studied enough.

The rocks of the Turonian layer in the northern regions of the Ternopil and Khmelnytsky regions are represented by pen chalk with a thickness of up to 44-90 m. The chalk is distinguished by its purity of composition and, in addition to its use as a carbonate component in the production of cement, it can also be used for the production of air building lime, but only under the condition of burning in special furnaces due to low mechanical strength.

In the southwestern part of the Ternopil region (in the basins of the Zolota Lypa, Koropets, Strypa rivers and in the upper reaches of the Seret river), chalk-like limestones of the Turonian stage are widespread, white, fine-grained, with flint nodules, 3–40 m thick. The limestones have a high content of calcium oxide and is a good raw material for burning lime.

Marls of the Konyak and Santonian levels are not widely distributed and are developed only in the northern and western parts of the Ternopil region. Their capacity varies from 2 to 20–40 m. They are not used as a building material within the region.

The main raw materials for the sugar industry, the production of lime and limestone flour in Podillya are rocks of the Neogene system. They are widely distributed and are represented by deposits of two levels – Baden and Sarmatian. The rocks of the Baden layer are known only in Ternopil, the Sarmatian – within all three Podilsk regions. They are represented by various limestones: detritus, shelly, serpulic, oolitic, lithothamnian, chemogenic, etc. The purest and most homogeneous in terms of physical and mechanical properties are the organogenic limestones associated with the Tovtry ridge. Therefore, the largest deposits of raw materials for the technological needs of the sugar industry and the production of high-quality lime are located within its borders. Horizontally layered limestones of the Middle Sarmatian (organogenic, oolitic, clastic) are less homogeneous in chemical composition and physical and mechanical properties and mainly serve as raw materials for obtaining building lime of various grades; the purest varieties can also be used in sugar production.

Freshwater rocks suitable for liming are also common within Podilsk Podnisteria – limestone tuffs (travertines). True, their reserves are much smaller compared to limestones of marine origin, but they are formed precisely in those places where calcium is leached from soils and rocks. Therefore, the deposits of these specific rocks are essentially reservoirs of calcium taken from the soil and ready for use. Travertines are essentially not developed at this time.

In Podillia, 25 deposits of carbonate raw materials for reclamation purposes have been taken on the State balance sheet. Today, only a few of them are being developed with insignificant volumes of production (90,2 thousand tons in 2020), that is, it can be stated that there is no demand for this type of raw material in conditions when large agricultural producers – collective farms and state farms – have ceased to exist. Modern farms are not yet able to allocate funds for the purchase of this meliorant, which, accordingly, does not stimulate investment in the development of explored deposits. In connection with the above, the deposits described below should be considered as a reserve fund of raw materials that should find application in the near future.

Table 2
The resource base of mining and chemical carbonate raw materials of Ukraine (according to the data of DNVP Geoinform of Ukraine)

|  | Number<br>of<br>deposits | They are being developed | Total stocks of raw materials (A+B+C1) as of January 1, 2021, thousand tons | Reserves<br>under<br>development,<br>thousand tons | Production<br>in 2020,<br>thousand<br>tons |
|--|--------------------------|--------------------------|---|--|--|
| Carbonate raw<br>material for<br>liming acidic<br>soils    | 37                       | 5                        | 90 732,5  | 6 580,5  | 93,2                                       |
| Carbonate raw<br>material for<br>feed additives            | 5                        | 2                        | 26 752,7  | 4 763,3  | 12,5                                       |
| Carbonate raw<br>materials for<br>sugar mills              | 14                       | 4                        | 323 193,6   | 24 029,8   | 1 777,8                                    |
| Carbonate raw<br>material for the<br>production of<br>soda | 4                        | 2                        | 109 236,9   | 51 625,9   | no data<br>available                       |

The state balance sheet for the Ternopil region includes 4 limestone deposits suitable for liming acidic soils: Bridok-Livoberezhny, Polupanivske, Monastyriske-1 and Torske. Total reserves for all deposits in categories A+B+C1 amount to 18 246 thousand tons (as of January 1, 2022).

Currently, 3 deposits are being developed.

*The Bridok-Livoberezhny deposit* is being developed for rubble and rubble by commercial structures and LLC Burdyakivskiy special quarry.

The Polupanivske deposit is being developed by the Production Company «Mining Industry» LLC also as raw material for sugar mills. Production in 2021 amounted to 128,3 thousand tons.

*The Torske deposit* with industrial reserves of 844 thousand tons is being developed by Dary Zemyi PE. There are no production data.

Currently, limestone flour in the region is obtained as a by-product from the waste of stone-crushing production in quarries where limestone is mined for rubble and crushed stone and for the sugar industry (*Polupanivskyi, Maksimivskyi, Galushchynetskyi, etc.*).

Ten deposits are known in the Khmelnytskyi region, the reserves of which are approved as raw materials for liming acidic soils. All deposits are small and concentrated exclusively in the southern part of the region.

*In the Karachkivets deposit*, which is listed as a reserve for the needs of the sugar industry, 2 115 thousand tons of reserves are estimated as raw material for mineral feeding of animals and poultry. Reef limestones, detritolithothamnia of Sarmatian age. One chalk deposit in the region has also been evaluated as a raw material for fodder applications.

11 small deposits of raw materials for liming acidic soils (10 limestone deposits and one chalk deposit) were explored in the Vinnytsia region. All deposits are located in the southern part of the region. Limestones are spread over a large area of the region – from the line Bar – Zhmerynka – Kryzhopil to its southern and western outskirts. The resources of raw materials are practically unlimited, and the quality in most cases meets the requirements of the standards for limestone flour. Grinding fairly dense limestones, however, is associated with significant energy costs and certain technological difficulties. Conditionally ground limestone flour in the region was produced by the only workshop of Sulyatsky Quarry Management, which was stopped in the mid-90s of the 20<sup>th</sup> century.

More rational, according to local experts<sup>10</sup>, is the use of flour, which is formed as waste when sawing wall blocks from shell limestone, because they are characterized by a very high calcium content, and the sawing process contributes to intensive grinding of the rock. Up to 20 thousand tons of such waste is generated in the region every year, and hundreds of thousands of tons are accumulated in tunnels and quarries.

It is also appropriate to use soft, thin-porous chalk-like rocks common in Transnistria for the liming of soils. Their  $CaCO_3$  content is 82-85%, they are easily crushed and interact more actively with the soil. There are also known deposits of chalk, which contains about 3% of citrate-soluble  $P_2O_5$  and acts simultaneously as a limestone meliorant and phosphorite flour.

 $<sup>^{10}</sup>$  Сивий М. Я., Паранько І. С., Іванов Є.В. Географія мінеральних ресурсів України. Монографія. Львів : Простір, 2013. 683 с.

### 3. Carbonate raw materials for the sugar industry

Mineral raw materials for sugar mills are strong and chemically pure carbonate rocks (limestones) with a CaCO<sub>3</sub> content of more than 93%.

The main indicators for determining the suitability of limestones for sugar production are their chemical composition and strength. Lime and carbon dioxide, which are obtained by burning limestone, are used to purify beet juice.

The requirements of the sugar industry for limestones are determined by the technical conditions DST 1451-90 «Limestone for the sugar industry» in force in Ukraine, according to which the chemical composition of the stone must correspond to the following indicators (in percent of dry matter): calcium carbonate content – more than 93; magnesium carbonate content – up to 2,5; the content of iron and aluminum oxides in the sum is up to 1,5; the content of alkali metal oxides (potassium and sodium) in the sum – up to 0,25; content of calcium sulfate – up to 0,3; the proportion of substances insoluble in hydrochloric acid is up to 3. Free admixtures of sand, clay, vegetable soil, pieces of weathered upper layers of limestone, etc. are not allowed. The compressive strength limit of the rock in the air-dry state should be over 100 kg/cm<sup>2</sup> 11.

Similar requirements apply to chalk, which is used for lime to purify beet juice:  $CaCO_3$  – more than 96%;  $MgCO_3$  – up to 1%;  $Fe_2O_3$ +  $Al_2O_3$  – up to 1%;  $CaSO_4$  – up to 0,05%;  $K_2O$ + $Na_2O$  – up to 0,25%;  $SiO_2$  – up to 2%.

Harmful impurities in limestone are considered to be: silica, which clogs the equipment and makes it difficult to filter the juice; gypsum, which forms scale and partially falls out of the solution together with sugar; alkalis, which cause the loss of sugar in molasses. Alumina, magnesium oxide, and iron oxide are considered ballasts that are completely precipitated at saturation, in addition, magnesium oxide colors the sugar in shades of gray.

Limestones that meet the requirements of the sugar industry are common in the southern part of the Volyn-Podilsky plate, on the southwestern slope of the Ukrainian shield, where they are confined to the cuts of the Miocene Baden and Sarmatian strata. The state balance of reserves includes 14 deposits, the total confirmed reserves of which are 323 193,6 thousand tons, of which four, with reserves of 24 029,8 thousand tons, continue to be developed (Table 2).

The main part of the balance reserves (70-75%) of high-quality limestone for the sugar industry is concentrated in the Tovtry ridge in the territory of Ternopil and Khmelnytskyi regions.

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<sup>&</sup>lt;sup>11</sup> Державний стандарт України «Камінь вапняковий для цукрової промисловості». Технічні умови. ДСТУ 1451-96. Київ: Держстандарт України, 1996. 4 с.

In the Ternopil region, only two limestone deposits, which are taken into account by the State Balance of Reserves, meet the conditions listed above: Polupanivske of the Skalat territorial community (TC) and Potutorske of the Berezhansk TC of the Ternopil district.

At the Polupanivske deposit, lithothamnium limestones of the Sarmatian age are mined, along the way serpul limestone, suitable for the production of crushed stone and lime, is mined.

The mineral in the deposit is gray limestone, recrystallized with an average thickness of 5,4 m. The overburden is represented by a soil layer, yellow-brown loam, and gray calcareous limestone. The ratio of overburden capacity and productive layer is 1:1,5. There is no groundwater at the deposit.

The content of CaCO<sub>3</sub> in recrystallized limestones is 94,3–96,8%, in recrystallized limestones it is 94,4–96,3%.

In addition to being suitable for the needs of the sugar industry, recrystallized limestones can be used for the production of limestone flour and the production of 400-grade crushed stone (including for road construction), which meets the requirements of MRTU 21-33-67 and the production of crushed stone with fractions of 5–10 mm, 10–20 mm, 20–40 mm for construction work.

Weathered limestones can be used for the production of building lime.

As of January 1, 2022, the approved reserves of the Polupanivsk deposit in categories A+B+C<sub>1</sub> are 54 472 thousand tons. In 2021, 294,8 thousand tons of stone were mined, the quarry is equipped with explored reserves with a design capacity of 154 years. The deposit is being developed by the Polupaniv branch of VK «Mining Industry» LLC.

The Potutorsk deposit of Turonian chalky limestones with reserves of more than 19 million tons is listed on the balance sheet as not planned for development and subject to write-off due to the low quality of raw materials.

Six deposits for the sugar industry have been explored in detail in the Khmelnytskyi region, and all of them are located in the two southern districts – the former Chemerivtsi and Kamianets-Podilskyi. Total reserves amount to more than 107 million tons, but only two fields are being developed. One deposit in the Chemerovetskyi district (Vyshnivchytske) has been previously explored and its reserves have not been confirmed. All deposits are confined to two Miocene reef ridges – Tovtrova and Eastern, buried under a layer of Quaternary and Sarmatian clays and also composed of Lower and Middle Sarmatian limestones. The last ridge stretches for 230 km, has a variable width, which varies from 8-10 km near the village. Kostyantyniv up to 30–35 km near the village of Tomashpil in the neighboring Vinnytsia region.

The thickness of the limestone varies within the zone, increasing in the southeast direction from 15 to 60 m.

Of the exploited deposits, only one – *Niginsko-Verbetskyi* produced 1 060,7 thousand tons in 2021. The total reserves in the deposits under development amount to 44 737,8 thousand tons. Almost the entire amount of production is provided by only two deposits – *Niginsko-Verbetske and Verbetske*.

Two fields in the region – *Bugaikha and Karachkivetske of Chemerovetskyi district* – are in reserve, but the first of them with explored reserves of more than 45 million tons will obviously be decommissioned because it is located on the territory of the Tovtry Reserve.

It should be noted that the solution to the issue of providing the sugar industry with calcareous raw materials, the expansion of raw material bases for its needs depends on the solution of the problem of the Tovtry ridge as a unique natural formation. It is about the development of a complex interdepartmental program for the protection of Tovtry while simultaneously providing the sugar factories of Ukraine with the necessary reserves of limestone according to the proposals of the Ministry of Ecology and Natural Resources of Ukraine. Moreover, the region is one of the main suppliers of carbonate raw materials for the sugar industry of Ukraine (limestone reserves make up 38,49% of the total in Ukraine).

The production of raw materials for the sugar industry can be significantly increased, firstly, due to the full utilization of the capacities of the operating quarries – Niginsky and Verbetsky; secondly, when the prepared Karachkivetsky complex field is put into operation, where limestone can be mined for the needs of animal husbandry. Increasing the reserves of this type of raw material in the region is possible after detailed exploration of the *Vyshnivchytsky* deposit, located 24 km from the station. For sale in a wooded area. The Opil limestones of the deposit are composed of lithothamnium-detrital, detrital varieties, recrystallized, strong. The total reserves, estimated according to category C<sub>1</sub>, amount to 76 400 thousand tons. Limestones can be used, in addition to the needs of the sugar industry, also for the production of building rubble and lime.

In the Vinnytsia region only two deposits for the sugar industry are taken into account. Their total reserves amount to 31 583 thousand tons (about 9.5% of the total in Ukraine). One deposit – *Studenivske* – is classified as large. In 2021, there was no mining at the deposits.

Despite the fact that the limestones lie in favorable conditions for mining, almost all deposits are located in the territory of the Podilski Tovtry National Nature Park, which raises the question of the liquidation of active quarries. Conducting exploration work within the Tovtry ridge, as the most promising

area, is strictly limited. From these considerations, it is clear that there is a problem of finding new promising areas and deposits of limestone raw materials, the quality of which would meet the established standards. Taking into account the fact that a long period of time passes from the beginning of searches to the introduction of deposits into operation, the issue of conducting geological exploration works on limestones for the technological needs of the sugar industry is urgent.

At the same time, new technologies for sugar production are being developed in order to reduce the need for limestone extraction and the use of fine-fraction limestone that has accumulated in landfills, where its quantity exceeds 30 million tons. The use of these reserves can ensure the uninterrupted operation of all factories in Ukraine for several years, as well as significantly reduce the man-made impact landfills on the environment in general and reduce soil and water pollution in particular. Another promising direction is the regeneration of lime from the filter sediment of sugar beet production. Today, about 8 million tons of filter sediment are produced annually at sugar factories, and only part of it is used in agriculture for liming acidic soils. This would make it possible to reduce the costs of limestone for the sugar industry by 70–75%.

In the Ivano-Frankivsk region, the promising *Horodyske* deposit with reserves of more than 25 million tons is being developed, but raw material production is low - 0.05 thousand tons in 2021.

The main enterprises that develop deposits that provide sugar factories of Ukraine with technological stone are PJSC «Podilsky Tovtry» (Niginsko-Verbetsk deposit), LLC «Ukrprombud» (Verbetske) and PJSC «Lopushnyanskyi karier» (Horodyske).

## 4. Carbonate raw materials for soda production

Carbonate rocks (limestones, chalk) with a high content of calcium carbonate (up to 98%) are suitable for use in the chemical (soda) industry. The main indicators of the suitability of carbonate raw materials for the chemical industry are regulated by GOST 12085-88 «Natural chalk, enriched», TU 6-18-216-75 «Limestone for soda ash», etc. The content of CaCO<sub>3</sub> (in the amount of 1,2% MgCO<sub>3</sub>) for crushed chalk is set in the range of 90...97%, for commercial chalk –  $96...98\%^{12}$ .

In Ukraine, four deposits of this raw material were discovered with total confirmed reserves of 109 236 thousand tons, but only two of them are being developed, the reserves of which amount to 51 625 thousand tons. These are

<sup>&</sup>lt;sup>12</sup> Державний стандарт України «Крейда природна збагачена». Технічні умови. ГОСТ 12085-88. Зміна № 1 (для застосування тільки на території України). Київ, 2007. 4 с.

the Raigorod and Bilohoriv deposits, which are related to the deposits spread in the northern and northwestern parts of Donbas strata of the Upper Cretaceous age.

The *Raigorod* deposit is located in the Sloviansk district of the Donetsk region. and has been in operation since 1847, and Bilogorivske is located 10 km northwest of Lysychansk. The first is the raw material base of the Slavyansk Soda Plant, and the second was developed by JSC Lysychanska Soda. The supply of Bilogorivsk quarry with chalk reserves suitable for soda production is approximately six years. Now the deposits are not exploited.

In the Ivano-Frankivsk region. *Dubovetske* deposit of limestone suitable for soda production was discovered, but at the moment it is not being developed either. The North Baksan limestone deposit with reserves of 52 869 thousand tons is located in Crimea.

There are no data on the production of raw materials in Ukraine in 2021.

#### CONCLUSIONS

The above allows us to state the following.

- 1. The main rocks used as raw materials for soil liming, feed additives, sugar industry and soda production in Ukraine are limestone, chalk and shell.
- 2. With the total number of deposits explored in detail and prepared for exploitation and significant reserves, the degree of their intended use is extremely low only 13 deposits are being developed with total reserves of 549 909 thousand tons and raw material production in 2020 of 1 883,5 thousand tons, which is not satisfies, in particular, the needs of sugar factories in technological raw materials.
- 3. The main obstacle to the expansion of the raw material base of this type of raw material (especially for sugar mills) is the location of numerous explored deposits on the protected lands of Podilski Tovtry and the impossibility of setting up exploration works there.
- 4. A real increase in reserves can be obtained by putting into operation some promising deposits Karachkivetskyi, Vyshnivchytskyi, and production can be increased if necessary at existing quarries (Niginsko-Verbetskyi, etc.), the production capacities of which are far from fully loaded, but all these measures are possible only under the condition of favorable market conditions (especially for ameliorant breeds).
- 5. Filter waste from sugar production, the use of fine-fraction limestone (screenings) accumulated in large quantities in limestone quarries, the use of limestone flour in tasse stone deposits, etc., can serve as an alternative to natural carbonate raw materials to a certain extent.

#### **SUMMARY**

The article considers aspects related to the spread in Ukraine, explored reserves and resources, the current state of use and prospects for increasing reserves and optimizing the use of carbonate mining chemical raw materials, which are used as a meliorant (for liming acidic soils), for fodder applications in feeding agricultural animals and poultry as technological raw materials in the sugar industry and soda production.

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# КВАНТОВО-ХІМІЧНЕ ДОСЛІДЖЕННЯ РЕАКЦІЙНОЇ ЗДАТНОСТІ ЕПІХЛОРГІДРИНУ ТА ОЛІГОМЕРНИХ ПРОДУКТІВ НА ЙОГО ОСНОВІ ПРИ ПРОМОТУВА́ННІ ПОЛІМЕРИЗАЦІЙНИХ ПРОЦЕСІВ

### Токар А. В.

### ВСТУП

Зацікавленість сучасних дослідників у розвитку хімії епоксидних сполук легко пояснюється з точки зору їх різносторонньої реакційної здатності, яка проявляється у взаємодії із численними електрофільними та нуклеофільними реагентами, а також у здійсненні мономолекулярних термічних та фотохімічних перетворень, що сприяють розкриттю епоксидного циклу або процесам фрагментації молекул. Таке розмаїття хімічних властивостей оксиранів дозволяє використовувати ці сполуки, так само, як і їх прямі гетероаналоги – азиридини та тіїрани, в якості