## https://doi.org/10.31713/m1303 FEATURES AND PROSPECTS OF THE USE OF VOLYNO-PODILLIA VOLCANIC TUFFS



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#### Abstract

The analysis of scientific research on the physico-chemical properties of tuffs of the Volyn-Podilsky Formation confirms their suitability for wide economic use. A theoretical analysis of the suitability of zeolite-smectite tuffs for use in many branches of the economy, in particular, in animal husbandry, poultry farming, plant breeding, medicine, for the production of sorbents for various types of intoxication, was carried out.

The tuffs of the Rivne region are products of the volcanic eruption of basaltic magma. They are composed of volcanic ash and sand, cemented and subsequently recrystallized under the action of hot underground waters. Tuffs in places have completely transformed into zeolite-smectite rocks, which contain a significant amount of useful components (MgO - up to 16%, N<sub>2</sub>O - up to 7.5%, K<sub>2</sub>O - up to 7.5%) and trace elements (iron, copper, titanium, cobalt and etc.).

The mineral composition of the tuffs of the Rivne Region was determined by experimental research.

Possible ways of their use are nature protection measures, which are very relevant for the ecology of the Rivne region, as well as agriculture and the construction industry.

For the effective use of Volino-Podillia tuffs, it is necessary to develop recommendations and normative documentation for their extraction and application, which requires further research of Volino-Podillia tuffs, clarification of their reserves in the region and determination of development sites.

#### Introduction

According to the requirements of the growth of requests and production needs, exploration and research of various, so far littlestudied breeds, with the aim of their further application in various fields, is becoming relevant. Basalt quarries are being developed within the Volyn-Podilsky platform. This rock was classified as a promising mineral (agrochemical raw material) and now a more detailed study of their physical and chemical properties will open new and new opportunities for their use. Currently, tuffs are used in construction, agriculture and for the purpose of using tuffs as collection stones, that is, for nature protection purposes. In the course of the work, various types of literature were used: reference, research, and specialized scientific literature containing new data on this topic, the comparison and comparison of which gives an idea of tuffs as a rock, occurrence, and the possibilities of their wide use.

The study of new objects will provide an opportunity to diversify the areas of specialization of production, to make it more economical and cheaper. The relevance of the work consists in collecting information on mineralogy for the systematization of the material, conducting field research at basalt quarries in the region, collecting samples of tuffogenic rocks, conducting chemical (laboratory) research with the aim of establishing their use in various branches of the economy of the Rivne region.

The object of the study is: Rafalivska basalt quarry, Berestovets quarry and Politsky quarry.

Subject of research: zeolite-smectite tuffs, minerals and rocks of basalt quarries.

Research methods: primary collection and processing of information from scientific research literature, field geological studies at basalt quarries, collection of actual material, practical studies in the mineralogical laboratory of the Shubkiv Research Station.

Purpose: to investigate the features of tufa rocks, their origin and the possibilities of use in various areas of the economy.

Main tasks:

- get to know and study tuffogenic rocks, collect collection material for laboratory research,

- to prove the value of using tufa rocks in the economy of the region.

- to find out which tuffogenic rocks can be used as a useful mineral, others as collection material.

- to present the results of laboratory studies on the influence of tufa rocks on soil fertility in the Rivne region.

#### 1. General characteristics of pyroclastic rocks

Tuffs belong to pyroclastic rocks, which are formed from solid volcanic materials - ash, volcanic sand. This volcanic material is thrown into the air during an eruption, transported by water and wind, and accumulates in areas adjacent to volcanoes [1-5].

Pyroclastic rocks have signs of both sedimentary and magmatic origin, so they are separated into a separate group. Their classification is based on a number of features, including the amount of pyroclastic material in the rock, the size of the particles, and their chemical composition.

Pyroclastic fragments, settling on the surface of the earth, form accumulations, often mixed with sedimentary rocks. If pyroclastic material is contained in an amount exceeding 90% - tuffite, from

10% to 30% - tuffogenic rock. Pyroclastic particles vary in size. Fragments with a diameter of 5 to 50 mm are called lapilli. The smallest particles, often invisible to the naked eye, are called ash (from 0.01 to 0.1 mm) and make up ash tuffs. During the deposition of ash and lapilli on low-lying areas together with sedimentary, detrital material, mixed deposits of pyroclastics with siltstone, sand and gravel particles - tuffites.

Particles from 0.1 to 5 mm are sand, forming granular tuffs. Larger fragments from 50 to 200 mm (and often larger) are called bombs, if at the time of their formation, they were completely or partially in a fragmented state as blocks, if they are represented by angular fragments of hard rocks. Rocks with a predominant content of bombs are called agglomerates, and are composed mainly of volcanic breccia blocks. With significant admixtures of ash in the latter, they are called tufobrekcias.

According to their composition, pyroclastic rocks can be liparite, trachyte, andesite, basalt. Ashes and tuffs can be further divided by the content of glass, individual mineral crystals and rock particles. The formations, which mainly include glass, are called wind ashes and wind tuffs. The windclastic structure is characterized by fragments of volcanic glass of curved, sickle-shaped, and rugule-shaped shapes and is widespread mainly among finely fragmented tuffs.

Rock fragments can range in size from ash to large blocks, while single crystals or their fragments are rarely larger than coarse ash or small lapilli. Glass particles come in different sizes, but mostly they are small. During a volcanic eruption, larger and denser particles are transported to shorter distances compared to smaller and, accordingly, lighter particles and accumulate closer to the source of their formation. Lapilli containing slag or pumice of low-density precipitate together with much smaller thermal particles represented by nonporous glass and crystals. At the same size, fragments of crystals and rocks tend to fall faster and closer together than less dense fragments of glass. Thus, in the deposits of one ashfall, denser lithoclasts, crystaloclasts, will be concentrated mainly in the lower part of the layer, and glass wool - in the upper part. Therefore, a single tuff sample may not accurately reflect the magma composition. The size of the particles in individual layers of one volcanic field also depends on the variation of the force of the eruption and the force of the wind [3, 6-10].

#### 2. Features and types of tuffs, their composition

As mentioned above, tuffs consist of fragments of igneous rocks, effusive rocks, and igneous minerals cemented by ash, rarely sedimentary material. The color of tuffs is diverse - white, gray, pink. Density 0.75-1.4 g/cm<sup>3</sup>. Porosity reaches 70%. The limit of compressive strength is from 8-10 to 70 MPa. Tuffs are poorly heat-conductive and frost-resistant, often have a pronounced layered structure. The dense, hard type of tuff is called tras, and the loose type is called puzzalan. The tuffs formed by aerial deposition have a sharply siliceous composition and are formed mainly by glassy ash and pumice lapilli. Few crystals of quartz, sanidine, sodium plagio-clase, or biotite are usually scattered among the glass fragments [3-5].

A special type of basaltic tuffs are the so-called shalsteins - shalelike, always underwater basic finely fragmented tuffs, which consist of pumice-like vesicular fragments of glass. The fragments do not contain eruptive crystals - pyroxene, olivine, plagioclase or contain them in very small quantities. The presence of flat lenses of vitreous fragments oriented in parallel planes and strongly stretched and flattened is characteristic of the chalsteine structure. The more bubbles in the glass of the shards, the more easily it flattens under the pressure above the accumulated masses, and the shards are easily drawn into thin "films" that envelop the crystals, which better resist crushing, and the clusters of calcite crystals that form in the binding mass.

If shalstein contains crystals of field slag, which withstands crushing well, then a crystallastic structure is created. Porous tuff material - chloritized glass - in such rocks stretches and envelops the feldspar grains that were preserved from crushing, creating a semblance of a fluidal structure.

When ash falls through clouds saturated with moisture, very thin wet particles can collect in the form of successive layers on some fragments, forming spheroidal ash balls - accretion lapilli, the diameter of which varies from 2 to 10 mm, but often there are larger ones. They accumulate relatively close to the center of the eruption. Accumulations of accretionary lapilli are called pisolitic tuffs. Deposits of very hot pyroclastic flows, which are also called tuffs of thermal flows, are called ignimbrite. Flows of this type move very quickly and their deposits are quickly formed at temperatures of 600- $900^{\circ}$ C. Some ignimbrites are the product of a single flow. But often they consist of many streams that moved so quickly one after the other that each previous stream did not have time to cool completely, and all the streams eventually solidified as one. In some cases, the power of some streams may not exceed 1 m, but there are those that occupy large areas reaching several hundred meters, especially if they fill the valley.

As the ignimbrite cools, it is rarely preserved as a mass of separate fragments. More often, hot particles of glass connect at the points of their collision and the entire flow is sintered. If there is no compaction of ignimbrite during binding, deformation of glass particles, initial welding is said. Such rocks often have a wind-clastic structure and are not strong enough, porous, easily broken into blocks. However, glass fragments are often deformed, more firmly welded together, and the mass is compacted. As a result, hard, relatively low-porous rocks are formed, pieces of glass are flattened while still hot, sometimes harder fragments of crystals are bent, lapilis and pumice bombs are flattened into disk-shaped lenses, which received the name fiame. In the cross-sections, it can be seen that in most of the fiame there are longitudinal dark veins or partitions former pores of pumice, which were closed as a result of compaction and welding. The degree of welding is so significant that lapilli pumice tuffs turn into dense glass, almost without pores and similar to obsidian.

Volcanic rocks formed as a result of magma fragmentation, if they were subjected to rapid hardening by water, are called aquagenic tuffs or hyaloclasts, which are formed most often when lava flows into the sea or into a freshwater basin. Hyaloclasts are mainly basaltic in composition and consist mainly of glass fragments bounded by smooth fracture surfaces. Their typical fragments are pure brown basaltic glass (sideromelane) without pores, in contrast to the highly porous vitreous or cryptocrystalline fragments (tachylites) characteristic of basaltic ashes and lapilli. But since basalt glass easily reacts with water, in most aquagenic tuffs it is at least partially transformed into a yellow or brown resinous substance - palagonite. Therefore, aquagenic tuffs can be recognized by the physical features of the glass particles. The chemical composition of palagonite is not stable, but it necessarily contains a lot of iron oxide. A palagonite tuff is formed, which, as it deepens, turns into smectite, which, in turn, turns into chlorite at a great depth. Relics of plagioclase, olivine, or pyroxene crystals are also present in many palagonite tuffs [5].

# 3. Volcanic tuffs of Volyn and their general petrographic characteristics

Considerable deposits of smectite and zeolite-smectite volcanic tuffs have been discovered in the Rivne region, which, thanks to their valuable physical and chemical properties, are suitable for wide economic use. According to deep geological mapping, tuffs are traced under the Mesozoic-Cenozoic sediments along the western slope of the Ukrainian crystalline shield in the form of a strip 1...10 km wide at depths from 5 to 250 m. The tuffs come to the surface in basalt quarries: Berestovets, Ivanova Dolyna, Politsi, Rivne region. Tuffs are laid down in layers, forming strata with a thickness of several meters to 140 meters [4].

The following types of pyroclastic rocks of the main composition are found in Volyn:

- agglomerate tuffs and slag tufobrekcias with bombs and lapilli;
- coarse-clastic-coarse-clastic (psephytic) tuffs;
- medium clastic (psamitic) tuffs;
- fine-grained (siltstone-pelitic) tuffs;
- tuffites and sandstones.

Agglomerate tuffs and slag tufobrekcias consist of coarse pyroclastic material, among which one can distinguish volcanic debris thrown out in a solid plastic or semi-liquid state. In the group of volcanic fragments thrown out in a solid state, the homogeneity of the composition and structure is revealed, and the fragments have an angular shape. The second group is characterized by figured outlines: pear-shaped, ellipsoidal, flattened shapes with twisting elements. The composition of basalt fragments is mostly olivine-free and, much less often, olivine-bearing. They are characterized by a variety of structures - from vitrophyric, hyalopilitic to intersertal or porphyry. Ruzhyl tuffobrekcias contain up to 85% of ruzhyl fragments. Their surfaces are oxidized or melted and have a micro-texture that is saturated with tonsils.

Agglomerate tuffs are cemented with ash material, as well as zeolites, chlorites and calcite. In many cases, partial sintering of fragments without significant deformation is observed. Coarse-, medium-, and fine-grained tuffs are composed of fragments of bubbly cherts, basalts, volcanic glass, and very rarely - fragments of intrusive traps and effusives of medium and acidic composition. Coarsefragmentary tuffs contain many fragments of cherts and basalts (40...97%) and therefore they are mainly represented by lithoclastic and windoclastic varieties. Volcanic glass fragments (60...70%) predominate in medium-clastic tuffs, and sometimes the content of cinder fragments increases significantly (up to 40...50%) (Rivna focal zone). It should be noted that the accumulation of corms is observed in the cross-section of any stratum not only among medium clastic, but also fine and thin clastic tuffs. Among the fine-grained and thinly fragmented tuffs, lithovitroclastic types prevail. The size of fragments of corms and various basalts in large and medium-fine fragmental tuffs does not exceed 1...2 mm. They have an isometric shape and structural and textural features do not differ from the bombs and lapilli described above.

Important features characterizing vitreous fragments include their shape and porosity. Based on these features, it is possible to determine which of the volcanic fragments were thrown out in a plastic state. Their gas cavities are elongated in the same direction as the fragments, causing the fluid-striped microstructure. This group is characterized by pumice-like microtextures [5].

In general, most of the investigated varieties of tuffs of the Rivne region have a mixed composition of fragments with the simultaneous presence of particles thrown out in a plastic, semi-plastic, and solid state. Unchanged vitreous fragments are observed relatively rarely. Some of them contain crystallites of the type longulites and belonites, as well as microliths, fragments with weak crystallization, liquid fragments of homogeneous glass. The indices of optical refraction of glass of yellowish-brown, green and black shades vary mainly from 1.5 to 1.58. Spectral analysis revealed chromium, titanium, vanadium, cobalt, nickel, manganese, copper, tin, zinc, lead and other elements in the glass fragments, the content of which does not exceed hundredths and thousandths of a percent.

The brownish-black fragments contain ore minerals: magnetite in the form of dust; hematite, which forms secondary films in cavities, on the surface of fragments, and iron hydroxides, which displace oxidized glass. The saponified vitreous fragments have an amorphous, crytocrystalline and crystalline composition, a heterogeneous greenish-yellowish shade with variable optical refraction indices.

The mineral composition of tuff cements is diverse. The most common are analcime and other zeolites, as well as chlorites, quartz, chalcedony and iron hydroxides. White analcime forms solid masses in cement. The chemical content of analcimes and basalts, diabases and tuffs is similar in composition. Their heating curves are also similar, and dehydration takes place in a relatively narrow temperature range of 200...400°C. Next to analcime, tuffs contain thomsonite in the form of creamy-pale-yellowish granular aggregates of radially radiating and spherulite composition.

Tuffites and tuff sandstones are most widespread to the southeast from the latitude of the city of Rivne. They are characterized by admixtures of terrigenous material from 10 to 25%, rolled and semirolled forms of fragments of volcanic origin. Ashy material, significantly altered to complete transformation into clay products.

The content of silica, iron oxides, magnesium, calcium, and alkalis change significantly in tuffs. The amount of water and volatile components increases sharply. These deviations are due to both postmagmatic and hydrothermal changes in the rocks and the ratio of basalt debris to cement, as well as its material composition, admixtures of terrigenous material, etc. In the freshest basaltic tuff, there is a similarity of compositions with average basalt.

#### 4. Areas of use of Volyn-Podillia tuffs

At present, many possibilities of their use in the economy are known: in the nature protection zone (reclamation of radioactive contaminated soils; purification of wastewater from NH4+), agriculture (fertilizer, plant nutrition stabilizer; feed additives, bedding with further use as fertilizer), construction industry (production of bricks, roof tiles and ceramic tiles; production of expanded clay; pigments for paints and colored concrete) [6].

Tuff deposits are almost always accompanied by deposits of valuable ore metals, in particular native copper; therefore, the exploration of new tuff deposits leads to the discovery of other, more valuable minerals. Experimental introduction of tuffs into radioactively contaminated sod-podzolic soils of the Rivne region has already shown the effectiveness of using these materials to reduce the isotope content in agricultural crops. Analcine-saponite varieties of volcanic tuffs are especially valuable in this respect. They are characterized by the highest content of zeolites (up to 40%) and smectites (up to 80%) and therefore exhibit the most sorption and cation exchange properties. An urgent problem for Ukraine and, in particular, for the Volyn-Podilskyi region, where the Rivne and Khmelnytsky NPPs are located, is the disposal of hazardous radioactive waste from the nuclear power industry. Underground disposal is defined as the most ecologically, technically and economically rational way of long-term isolation of all RW from the ecosphere.

The choice of a geological object for underground disposal is regulated by the following basic requirements regarding the economic feasibility and reliability of radioactive waste isolation: proximity of the object to sources of radioactive waste, high insulating properties of rocks and their sorption capacity in relation to radioactive isotopes, positive engineering and hydrogeological conditions of the territory cemetery Volcanic tuff layers of the Volyn series of the Lower Wend best meet these requirements.

The territory of the distribution of tuffs generally corresponds to the Volyn-Podilsky plate, which developed stably in a passive geodynamic regime for about 100 million years. The tuff bodies, undisturbed by tectonic dislocations, are tens of kilometers in area and have a thickness of up to 80-140 m.

Volcanic tuffs of Volyn-Podillia are waterproof and poorly permeable rocks. However, the possibility is not excluded that under the conditions of deep lying along the fractured zones, the pressure waters of the Gorbashiv aquifer may flow through them. In the presence of water, the primary minerals of tuffs are displaced by secondary smectites, which are capable of sorbing radionuclides and at the same time close microcracks and pores of rocks, as they occupy a larger volume than primary minerals [5].

The potential possibility of penetration through tuffs of fractured waters, despite all their conservation and sorption properties, significantly lowers the level of safety of RW burial in it. Therefore, the identification and study of such relatively dry tuff massifs in the Volyn-Podilskyi region should become an important task of future geological research and requires comprehensive engineering-geological, hydrogeological research on the subject of unconditional reliability of their insulating properties. But even now, a preliminary assessment of the insulating and sorption properties and the conditions of occurrence of the Volino-Podillia tuffs shows their high potential suitability for the burial of radioactive waste in a wide range of depths.

The positive mineralogical, physico-chemical and ecological properties of tuffs of the Volyn series, in particular their high ability to sorb radionuclides, significant specific surface area and water absorption index, low density and hardness allow considering this raw material as a useful mineral that can serve as an ameliorant of radioactively contaminated soils. At the same time, due to the high content of magnesium and lime-alkaline components, as well as the high content of a number of agronomically valuable trace elements, these rocks are potentially suitable for application to the soil as a complex natural mineral fertilizer and soil deoxidizer. Also, tuffs can be used for the production of saponite flour, which will increase the productivity of man-made and radioactively polluted soils, purify liquid food products from heavy metals and radionuclides, as a mineral admixture for livestock and poultry feed, etc.

As a result of intensive secondary processes due to pyroclastic and tuff-sedimentary rocks, deposits of kaolin, bentonite clay, alunite, mineral paints, etc. [4,5].

#### 5. Research results

An important property of tuff (Fig. 1) is that zeolite tuff has a high absorption selectivity and the ability to separate ions and molecules of various substances by size, as well as fairly high mechanical and chemical resistance. High porosity, compared to quartz sand, provides an increase in the capacity of harmful substances, therefore it has a higher ion exchange selectivity compared to a number of chemical elements, the content of which is strictly regulated. This is especially important in relation to the selectivity of radioactive elements, sorption capacity to heavy metals, phenol, ammonium nitrogen found in waste. Zeolite tuff cleans water by 30-40% better from microorganisms, from colloidal particles of mineral and organic origin. Tuffs have the ability to adsorb ammonia from the air, and therefore it is advisable to use them for deodorization of waste storage areas or production areas. It was established that 1 kg of zeolite tuff can adsorb up to 100 g of ammonia [3].



Fig. 1. Tuffs

Thus, the ion-exchange properties of tuff are used in the following cases:

1. To extract  $NH_4$  from municipal and technical waters. Klinoptilolite tuff is used to obtain ammonium, cesium, and phosphorus from wastewater.

2. To remove heavy metals from technical waters, in particular lead, chromium, cadmium. For cleaning acidic mine waters (2<pH<3) from metals Al, Ca, Cd, Co, Si, Fe, K, Mg, Mn, Na, Ni, Pb, Zn.

3. To extract radionuclides from the wastewater of nuclear power plants, where tuff is used as a cation exchanger to capture isotopes of cesium and strontium. For example, a type of tuff, mordenite, captures up to 98% of  $Cs_{147}$ .

4. For separation and capture of gases. For example, to extract  $SO_2$ , clinoptilolite tuff is activated with a solution of hydrochloric acid and used to capture  $SO_2$  from the gases of factories that produce sulfuric acid by burning sulfides.

5. To use zeolite as a catalyst, for example, in petrochemicals. At the same time, catalytic centers can be created in zeolite without activating other components. Clinoptilolite tuff is the only zeolite in which acidic centers are not formed during acetylene hydration, which are undesirable during catalytic transformations. High rates of benzene recovery when using this tuff. The absorptive capacity of the tuffs of the Rafaliv deposit of the Rivne region compared to other deposits is shown in table 1[6].

Table 1

Place of crea- tion	Cation ex- changeable ability	Na <sup>+</sup> g/kg	H <sup>+</sup> g/kg	NH4 <sup>+</sup> g/kg	Pb <sup>+</sup> g/kg	Cs <sup>137</sup> %	Pb <sup>2+</sup> g/kg	Hg2 <sup>2+</sup> g/kg	Zn <sup>2+</sup> g/kg		Си <sup>2+</sup> g/kg	Co <sup>2+</sup> g/kg	Mπ <sup>2+</sup> g/kg
Tendzamske (Georgia)	109	54	75	45	119	97	175	380	57	94	58	62	61
Shelves (Rivne region) обл., Україна)	118	57	79	48	162	99,5	179	420	62	97	65	60	75

Absorption capacity of tuffs

6. On the basis of mineralogical analysis, it was established that the content of zeolites in the tuffs of Politskyi quarry is about 43% of smectites and fine-dispersed iron materials, from 16% to 32%. X-ray structural and thermal analyzes showed that these tuffs contain 65% smectites and up to 28% analcime. In the Berestovets quarry in this region, an average of 65% of smectites were found.

The presented results of the quantitative analyzes showed that according to the content of petrogenic minerals, the volcanic tuffs of the Rivne region are altered and represented by zeolite-smectite rocks (Fig. 2), which have undergone significant secondary transformations and hydrothermal mineralization.



Fig. 2. Zeolite smectite tuff



Fig. 3. Rafalivka quarry

The conducted studies allow purposeful and effective use of tuffs. Of particular interest are the data on the average composition of trace elements in tuffs in three deposits. In the table 2 shows the average content of microelements in tuffs of three quarries of the Rivne region (Fig. 3), their correspondence to Clark values and maximum permissible concentrations (MPC) in soils.

The study of the results of these studies of trace element composition showed that tuffs cannot be regarded as basalt mining waste, but are a valuable mineral raw material that requires development and a comprehensive approach to its processing to extract useful metals and silicates.

The tuffs of the Berestovets quarry have two varieties that differ in composition. Under the basalt layer in the quarry, argillite-like siltstone tuffs with a thickness of 1-5 m lie. Deeper along the section, more granular psammite and psephyte tuffs lie. Siltstone tuffs contain an average of 65% of smectites, iron hydroxides, contain a high concentration of barium, vanadium, copper, and zirconium (see Tables 2, 3) [7].

Today, the tuffs of the Politsky deposit have been studied more fully in terms of geology and industry. Their deposits, the so-called saponite clays, have been explored and prepared for research and industrial development. They include a high content of saponites (up to 80%) and therefore show valuable sorption and cation exchange properties. These tuffs are characterized by high magnesium content (MgO - up to 11.6%) and high content of trace elements such as copper, chromium and zinc. An important factor is the absence of such elements as arsenic, mercury, and selenium in these tuffs, which are ecologically dangerous [8-10].

Table 2

The average composition of trace elements in tuffs by quarries, %														
Elements	Р	Pb	Ba	Mo	Sn	Си	Zn	Ni	Zr	Co	Cr	V	Мп	Ti
Rafalivka quarry														
Average value	670	5	350	0,8	5	103	46	35	140	31	47	116	1240	5480
Clarks	1500	6	330	1,5	6	87	105	130	110	48	170	250	1200	8000
MPC	-	30	-	-	-	100	100	100	-	-	100	150	1500	-
Berestovts quarry														
Average value	600	6	8000	1,0	2	300	40	25	200	25	30	400	600	6000
Clarks	1500	6	330	1,5	6	87	87	130	ПО	48	170	250	1200	8000
MPC	-	30	-	-	-		100	100	-	-	100	150	1500	-
Politsky quarry														
Elements	Cr	Ni	Си	Zn	Re	Sr	Y	Pb	Th	Ba	Ge	As	-	-
Average value	150	19	75	104	32	168	23	118	3	320	2	0,1	-	-
Clarks	170	130	87	105	60	470	21	6	4	330	1,5	2	-	-
MPC	100	100	100	100	-	-	-	30	-	-	-	2	-	-

The average composition of trace elements in tuffs by quarries, %

The name of the elements Rafalivka quarry Berestovts quarry Politsky quarry 3.0 Aluminum 0.03 10.2 30-32 57.2 42.0 Silicon 0.15 Phosphorus 0.1 0 Sulfur 0.3 1.2 0 Potassium 1.3 2.4 4,8 6.4-12.1 15 37.5 Calcium Titanium 2.8-4.0 1.3 0.5 Chrome 0.2 0.05 0.10.070 0.12 0.07 Manganese Iron 48-50 12.8 7.0 0.2 0.1 0.01 Nickel 0.4 - 0.7Copper 0.170.6 - 1.01.2 Zinc 0.05 0.07 Strontium 0.07-0.1 0.07 0.07

Content of elements in tuff samples from different quarries Concentration, %

Table 3

#### Conclusions

1. The analysis of scientific research on the physicochemical properties of tuffs of the Volyn-Podilsky formation confirms their suitability for wide economic use. A theoretical analysis of the suitability of zeolite-smectite tuffs for use in many branches of the economy, in particular, in animal husbandry, poultry farming, plant breeding, medicine, for the production of sorbents for various types of intoxication, was carried out.

- In agriculture - as a mineral fertilizer, seed preservation, animal and bird feed additives, plant nutrition stabilizer.

- In environmental protection activities - amelioration of radioactive soil contamination, underground burial of poisonous substances, wastewater treatment.

- In construction - production of building materials (bricks, roof tiles, ceramic tiles), production of cement and expanded clay, pigment for paints and colored concrete.

- As binding materials - ore wrapping, fertilizer wrapping.

2. It has been established that the tuffs of the Rivne region are products of a volcanic eruption of basalt magma that occurred approximately 600 million years ago. They are composed of volcanic ash and sand, cemented and subsequently recrystallized under the action of hot underground waters. Therefore, the tuffs in places have completely transformed into zeolite-smectite rocks, which contain a significant amount of useful components (MgO - up to 16%,  $N_2O$  - up to 7.5%,  $K_2O$  - up to 7.5%) and trace elements (iron, copper, titanium, cobalt etc).

3. The mineral composition of the tuffs of the Rivne region was determined by experimental research.

On the basis of mineralogical analysis, it was established that the content of zeolites in the tuffs of Politskyi quarry is about 43% of smectites and finely dispersed materials from 16% to 32%. X-ray structural and thermal analyzes showed that these tuffs contain 65% smectites and up to 28% analcime. On average, about 30% of smectites were found in the Rafalivskyi guarry. In the Berestovets guarry in this region, an average of 65% of smectites were found. The tuffs of the Berestovets quarry have two varieties that differ in composition. Siltstone tuffs contain an average of 65% of smectites, iron hydroxides, contain a high concentration of barium, vanadium, copper, and zirconium. Today, the tuffs of the Politsky deposit have been studied more fully in terms of geology and industry. Their deposits, the so-called saponite clays, have been explored and prepared for research and industrial development. They include a high content of saponites (up to 80%) and therefore show valuable sorption and cation exchange properties. These tuffs are characterized by high magnesium content (MgO - up to 11.6%) and high content of trace elements such as copper, chromium and zinc. An important factor is the absence of such elements as arsenic, mercury, and selenium in these tuffs, which are ecologically dangerous. During the writing of the research work, a number of laboratory and practical studies of zeolite-tufogenic rocks of the Rivne region were conducted. Prospective directions of their use in the economy of Ukraine have been determined.

4. Possible ways of their use are nature protection measures, which are very relevant for the ecology of the Rivne region, as well as agriculture and the construction industry. Together with the reclamation of radioactively contaminated soils and wastewater treatment, it is economically and ecologically appropriate to directly use the Volyn-Podillia tuffs as a potential site for radioactive waste disposal. Despite their great economic importance, at present the volcanic tuffs of the Volyn series are practically not used. In the basalt quarries of the Rivne region, they are dumped in huge volumes into dumps, hindering mining operations and creating man-made "lunar" landscapes. With a new approach to the study and use of smectite and zeolite tuffs as a new type of mineral resources, prospects for their complex extraction together with basalts for further processing and multi-purpose use are opening up.

5. For the effective use of Volyn-Podillia tuffs, it is necessary to develop recommendations and regulatory documentation on their extraction and application, which requires further research of Volyn-Podillia tuffs, clarification of their reserves in the region and determination of development sites.

#### References

1. Z. Malanchuk, V. Zaiets, L. Tyhonchuk, S.ana Moshchych, G. Gayabazar and Ph. Thao Dang (2021). Research of the properties of quarry tuff-stone for complex processing. E3S Web of Conferences. Volume 280 (2021) 01003, DOI:https://doi.org/10.1051/e3sconf/202128001003

2. Malanchuk E.Z. Efficiency determination of using magnetic separation during processing of basalt raw material. Coll. of science pr. Progressive technologies of coal, coalbed methane, and ores mining.– London: CRC press Balkema book.-2014.- c 71-75.

**3. Malanchuk** E.Z. Scientific justification of the technology of complex processing of metal-containing raw materials in the development of basalt deposits. autoref. thesis ... Dr. Tech. Sciences: 05.15.09. National Academy of Sciences of Ukraine, Institute of Geotechnology mechanics named after M.S. Polyakova, Dnipropetrovsk, 2015. p. 39.

4. Zeolite-smectite tuffs of the Rivne region: biological aspects of use / [Bogdanov G. O., Mandigra M. S., Melnychuk V. G. and others]; under the editorship MP Magpies. - Rivne: Volynski oberegy, 2005. - 184 p. 5. Melnychuk V.G., Mateyuk V.V. Volcanic tuffs of Volyn-Podillia as a new type of mineral resources // In the book. Problems of rational use, protection and reproduction of the natural resource potential of Ukraine. Theses add. 2nd All-Ukrainian Scientific method. conf. – Chernivtsi, Ruta, 2000. – P.133-134.

6. Protection against landscape pollution by household waste and industrial waste based on the use of natural sorbents. / V.A. Stashuk, Z.R. Malanchuk, A.M. Rokochynskyi, M.O. Klymenko, R.V. Zhomyruk, S.Yu. Gromachenko. / Edited by V.A. Stashuka, Z.R. Malanchuk and A.M. Rokochinsky. Monograph: – Kherson: 2014. – 420 p.

7. Minerals of the Rivne region. In the book Reclamation and development of the Ukrainian Polissia. Malanchuk Z.R., Korniyenko V.Ya., Malanchuk E.Z., Zhomyruk R.V., Ignatyuk I.Z., Malanchuk L.O., Moshchich S.Z., Solvar L.M., Tymoshchuk I .I., Romanchuk S.S., Zagurovskyi V.N. Collective monograph / edited by Doctor of Science, Professor, Acad. NAAN Ya.M. Gadzal, Ph.D., professor, member-cor. NAAS V.A. Stashuk, Ph.D., Professor A.M. Rokochinsky. – Kherson: OLDI-PLUS, 2018. – Volume 2. See 57. – 854 p. 600-617

8. Efficiency of using magnetic separation for the processing of metalcontaining basalt raw materials. Topical issues of resource-saving technologies in mineral mining and processing. **Malanchuk E.Z. Malanchuk Z.R. Korniyenko V.Ya.** Multi-authored monograph. – Petroşani, Romania: UNIVERSITAS Publishing, 2018. – 270 p., 65-89 pp.

9. Improvement of technological parameter of the technology of production of zeolite-smectite tuffs. **Malanchuk Yevhenii, Sergey Stets, Korniyenko Valerii, Marchuk Roman.** Sustainable development of resource-saving technologies in mineral mining and processing. Multi-authored monograph. – Petroșani, Romania: UNIVERSITAS Publishing, 2019. - 400 pp., 244-265 pp.

10. **Malanchuk Z. R.** Justification of the prospects for innovative development of the enterprise for the extraction of copper-containing basalts / Z. R. Malanchuk // Resource-saving technologies of raw-material base development in mineral mining and processing : multi-authored monograph. – Petroșani, Romania : UNIVERSITAS Publishing, 2020. – PP. 6-33.