# ГЕОЛОГІЯ

#### UDC 533.411

M. Mizernaya, Cand. Sc. (Geol.-Min.), Assoc. Prof., A. A. Khairullina, Cand. Sc. (Tech.), Z. I. Chernenko, Cand. Sc. (Geol.-Min.), E. V. Teut D. Serikbayev East Kazakhstan State Technical University, Ust-Kamenogorsk, Kazakhstan, e-mail: mizernaya58@bk.ru

### BASIC GUIDELINES FOR EAST KAZAKHSTAN SCHUNGITE USING

М. О. Мізерна, канд. геол.-мінер. наук, А. А. Хайрулліна, канд. техн. наук, З. І. Черненко, канд. геол.-мінер. наук, Є. В. Теут Східно-Казахстанський державний технічний університет імені Д. Серикбаєва, м. Усть-Каменогорськ, Республіка Казахстан, e-mail: mizernaya58@bk.ru

# ОСНОВНІ НАПРЯМИ ВИКОРИСТАННЯ ШУНГІТІВ СХІДНОГО КАЗАХСТАНУ

**Purpose.** Improvement of strength properties of concrete and corrosion properties of fine carbonaceous materials shungite.

**Methodology.** Field studies within the Bakyrchik ore field in Eastern Kazakhstan, sampling shungite rocks to determine the chemical composition and distribution patterns of the main minerals and impurities were applied. Electron microscopical studies of cement stone formation there were used. Research studies were carried out concerning the impact of shungite additive on endurance of cement stone against corrosion due to the impact of shungite powder on density of cement stone.

**Findings.** Shungite concentrates obtained from shungites of Bakyrchik deposit are promising for use as fillers of anticorrosion concrete, paints and varnishes. Integrated use of gold-and shungite raw materials opens up new prospects for the economic development of unique reserves of gold-fields of East Kazakhstan and stocks shungite not used yet.

**Originality.** It was proved that shungite powder used as a pigment and filling material improved anticorrosive properties of varnish-and-paint materials.

**Practical value.** This will significantly reduce the amount of man-made waste containing contaminants and polluting the air, soil and groundwater in the areas of development of gold deposits. The importance of the study is proved by shortage of new construction materials with anti-corrosion properties. These studies will make it possible to create entirely new materials with desired properties for the construction industry in Kazakhstan

Keywords: shungite, concrete, corrosion resistance, gold-sulphide deposits

**Introduction.** Shungite, unique in its properties complex carbonaceous feed, is widely used nowadays in different spheres and industries of foreign countries and especially in Russia. Shungite rocks are hardly used in Kazakhstan and are considered mostly theoretically.

Variety of shungite properties determined by their mineralogical and structural condition defines a great number of opportunities for using them in the national economy. Nowadays, a lot of research studies concerning the use of shungites are actively carried out in Russia, the USA, France, Japan and in Ukraine. The information concerning shungites application technology and their retinues is published and thus the market of goods and issues on the basis of shungites is being formed.

The word shungite is mostly associated with shungites of Karelia in reading matter. They were found in the 1960-s of the past century in black-shale Upper Proterozoic formations. However, natural carbonic formations containing minerals of shungite group (kerite-anthraxolite-shungite) are widely spread. Nearly all found occurrences of shungite – anthracolithic mineralization (except Russia and Kazakhstan) are of mineralogical interest. Commercial shungites formations are found in the south of Kazakhstan especially within extension of East Kazakhstan black-shale band where according to pre-

<sup>©</sup> Mizernaya M., Khairullina A.A., Chernenko Z.I., Teut E.V., 2017

diction estimate only gold-sulphide deposits of West Kalba contain about 530 million tons of shungites. Total predicted resources of this valuable raw material exceed the reserves of the only well investigated and exploited Zazhoginsky deposits (Russia, Karelia) by at least a hundred times. It enables to form new mineral resources base scarce carbonaceous feed.

In recent years perspectives of shungite black-hale formations of West Kalba have been estimated by the researchers of D. Serikbaev EKSTU. According to tentative forecast they made up more than 530 million tons of carbonaceous feed with organic carbon content from 4 up to 20 % and more. These reserves are rather compatible with the only well-investigated and exploited Zazhoginsky deposit (Russia, Karelia). It enables to form new mineral resources base of scarce carbonaceous feed.

Peculiarity of shungite formation occurrences in East Kazakhstan is their localization in zones of sulphide mineralization of gold-sulphide deposits of West Kalba. Besides, shungite-containing rocks form unique "envelopes" at a distance of 2-5 metres from gold-sulphide ore bodies (Starova L. G.) and they go to dumping site together with overburden during gold deposit development.

Complex usage of gold-sulphide and shungite raw materials will open a prospect for profitable exploration of East Kazakhstan gold-sulphide deposits, which are unique in reserves, and still unusable reserves of shungite rocks. It will enable significantly to reduce the amount of technogenic waste containing harmful adulterations that are dangerous for the air, soil and groundwater in the regions of gold ore deposit development.

The fields of shungite concentrates research applications are extremely wide and there are great perspectives for further research in different directions:

- high-carbon concentrates can be applied in production of non-stick paste as pigment and substitute of graphite in foundry production, substitute of technical graphite in rubber mix rubber mix including the production of tyres;

- concentrates with different ratio of shungite group minerals for using them in hydrometallurgy processes during bioleaching and acid leaching of rebellious and resistant ores;

- shungite concentrates for production of constitutional and corrosion resistant materials and compositions, mastics, varnishes for protection of equipment and different building constructions from influence of aggressive gases, acids;

- fillers for filters for cleaning industrial gases and waste waters;

- concentrates with average content of carbon for production of electrically conductive brick and concrete etc.

**Presentation of the main research.** The problem of longevity of buildings, constructions, building materials and building structures is studied by specialists from all over the world who are engaged in research, development, designing and building construction projects. The issues of endurance and longevity of building materials and structures are constantly considered at international

conferences concerning cement chemistry, concrete technology, application of fine-grained filling materials, at conferences concerning building and longevity of buildings and constructions. The important place is taken by the issue of concrete corrosion and its protection from corrosion.

Corrosion resistance of concretes on portland cement began to be studied at the same time with the studying of the processes of this cementing material hardening. As cement quality improves and as the knowledge on processes going on in the cement – water system becomes deeper, there appears necessity to study corrosion processes and resistance of cement stone compounds to different impacts. The structure of cement stone is negatively influenced by fresh water, aquosystems, hard fine-grained substances that can form interburdens from molecular and colloidal solutions.

The properties of aggressive media and conditions of their impact on building structures are quite various. One of the most difficult issues in studying corrosion processes is concrete corrosion in sulphate media. It is especially relevant for industrial enterprises of East Kazakhstan region such as JSC "Kazzinc", JSC "Ulba", JSC "UKTMP" and others.

Until recently basic protection method of concrete from sulphate corrosion was considered to be reducing aluminate phase content in cements, that is included in ettringite structure, and this provides high longevity of concrete. However recent research studies proved insufficiency of this condition for concrete protection.

Nowadays increased endurance of concretes to corrosion processes is achieved by the range of technologic measures, and one of these measures is production of highly dense concrete.

Laboratory studies of anticorrosion properties of compositions on the basis of shungite concentrates were carried out with a large amount of experimental material using complex of up-to-date methods. During this stage the research studies were carried out concerning the impact of shungite additive on endurance of cement stone against corrosion due to the impact of shungite powder on density of cement stone.

Cement of "Bukhtarma cement company" Heidelberg Cement  $\Pi \coprod 400 \amalg 20$  was used as bonding material. Real activity of cement was determined by standard methods (430 kgs/cm<sup>2</sup>) and on the equipment "Cement-prognoz" and equalled 427 kgs/cm<sup>2</sup>.

Granite macadam with fraction of 5–10 and sand with the fineness modulus  $M_k = 2.66$  were used as fillers. They corresponded to State Standards 8736 of the enterprise "Plant of nonmetallic materials" Ust-Kameno-gorsk.

Shungite powder was used as researched additive, its chemical composition was defined by the quantity of basic oxides in per cent due to mass, by X-ray fluorescence analysis method and represented as:  $SiO_2 - 57.2-59.0$ ;  $Al_2O_3 - 10.8-11.3$ ; CaO - 11.0-13.6;  $Fe_2O_3 - 3.5-7.5$ ;  $K_2O - 6.4-8.5$ . Specific surface area was 10000 cm<sup>2</sup>/g. Superplasticizing agent C-3 was used in the work.

Analysis of original raw materials and cement compositions was carried out both by standard methods and with the usage high-information physical-chemical methods. The ultimate composition of raw materials and structural analysis of cement stone samples, cement mortar and concrete was carried out on scanning-electron microscope JSM-6390-LV. Specific surface area of materials was defined by the equipment  $\Pi$ CX-10 A, accuracy  $\pm 1$  cm<sup>2</sup>/g.

As it is known concrete compression resistance and development of strength kinetics depend on conditions of formation and solidification of consolidated concrete mix that has been rationally selected by composition and thoroughly mixed. Besides basic components, special extra additives can be put into the concrete mix compound, including those ones from mineral raw materials [1]. Mineral additives have different mineral compound and dispersiveness, that is why they influence differently on concrete mix. It defines the field of application [2]. Due to use of such extra components that have an effect on volume concentration of cement stone in concrete there is the opportunity to produce concretes with special properties. For instance, disperse active and nonreactive mineral additives (fillers and micro-fillers) improve the structure of concrete on microlevel [3].

In this respect the studies were carried out to find out the influence of shungite powder adding and water-cement ratio on kinetics of cement stone strength gain. When cement stone compression resistance was defined, cube samples of  $20 \times 20 \times 20$  mm were used. Sample curing was carried out at temperature of 20 °C. Endurance was determined according to State Standards 10180-90.

Loading speed of samples was 0.4–0.6 MPa/s. Every sample party was tested at the age of 28 days. Test results (Fig. 1) showed increase in cement stone endurance from 5 to 10 % when shungite powder was added.

In this connection the role of additives is demonstrated in up-to-date concrete technology. The significance of cement paste rheological modification mechanism is highlighted. Special attention is given to cement composite water gain. Quick water gain causes water deficit for components of cementing material, and required technical properties (namely density) cannot be achieved [4]. It should be noted that cementing material is described in technical literature; its solidification is not connected with chemical interaction with water.



Fig. 1. Influence of shungite on endurance of cement stone

The alternative material for portland cement is geopolymer binder or geopolymer which is more well-known in the western scientific-technical literature. However, at the present moment the production and use of this binder are limited by technical troubles [5]. Moreover, studying of the issue concerning the effect of mineral additives on the process of cement paste water gain is going on. Thus, the effect of ground slag additive of 0-75 % on water gain was studied while using a superplasticizing agent and without it. It was noticed that ground slag added to the "cement+water" system is adsorbed on the surface of portland cement minerals and thus contributes to reduction of water gain. However, hydration stoppage of cement paste is observed in the presence of the superplasticizing agent. The stated aim of the research was to find out influence of adding shungite concentrates on the speed of cement water gain. The data obtained during the laboratory tests proved that addition of shungite powder improves water-holding capacity and consequently contributes to the increase in endurance and density of the hardened cement stone. Research studies carried out at this stage enabled to give quantitative estimate (Fig. 2) to relationship of water gain and amount of shungite added to cement. The additive was dosed as percentage of cement mass. Complete water gain period was characterized by the time passed from the beginning of the experiment to the end of water gain process. The best results were registered when 10 % of shungite powder was mixed in the compound of cement system; water-holding capacity exceeded 90 % (Fig. 2).

Significant increase in set strength with shungite can be explained from the position of physical and chemical interconnection of fine-grained shungite with the cement hydration products and formation of hydrafed calcium carboaluminate crystal which can serve as "nucleus of crystallization" and good epitaxic substrate for formation of new compounds.

While the reaction goes on, water indissoluble crystalline hydrates are formed which fill pores, capillary and fissures of concrete up to 0.5 mm, as well as prevent water filtration even if there is high hydrostatical pressure. Furthermore, formed crystalline hydrates become



Fig. 2. Influence of shungite on water-holding capacity of cement

the component of the concrete structure that compact it. When new portions of water appear in cement stone, the process of crystal formation restarts and concrete gains self-healing capacity.

According to the research data it was found out that new growths in cement stone are calcium aluminate sulfate hydrate of the following compound  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \times$  $\times 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$  (ettringite) or  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \times$  $\times 12\text{H}_2\text{O}$ . Ettringite is of particular interest which is formed with volume increase by 1.5-3 times in comparison with hydrated calcium aluminate of the compound  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  on the basis of which it is formed. Ettringite can play both constructive and deconstructive roles in cement stone. Constructive properties of ettringite are as follows, it is indissoluble in water and pores filled with it are in the shape of dendritic crystals complexes and they make proof against water. As for concrete, it keeps water-vapour impermeability.

Cement stone destruction under ettringite influence is due to increase in its volume while crystallization of aluminate sulfate hydrate. Destructive role of ettringite can be significantly reduced due to addition of shungite powders when concrete surfaces are treated with the methods of secondary protection (membranes and treatments).

To determine optimal quantity of shungite powder addition into cement concretes the following compounds were taken (Table 1): 1 compound of concrete – model, without additives; 2-5 compounds – with addition of shungite 5, 10, 15 and 20 % of cement mass – (addition of dry shungite and with tempering water).

The tests proved that method for shungite powder addition does not significantly influence strength characteristics of concrete. Furthermore, maximum increase in concrete strength is observed when 5 % of shungite powder is added (Table 2). If the amount increases, concrete strength decreases (Fig. 3).

It can be explained by the fact that addition of the stated amount of shungite enables to form skeleton frame with minimal intergranular porosity between cement grains. Besides, water demand of cement paste increases when introduced additive increases.

As shungite is the carrier of active centres and distributed in the volume of concrete regularly, under the condition of optimal dosing they provide multilevel structure arrangement activating the mechanism of selfreinforcement.

Predominance of dispersive and stable hydrosilicates contributes to the increase in strength and density of crystallization structure phases and determines connection between longevity and phase and porous parameters of cement stone structure.

The research results allows us to conclude that microreinforcing particles with the diameter up to 20 mcm can increase elastic limit and strength of concrete in the result of interpenetration of microfissures. The most significant work at this stage is that of cement matrix, in which shungite particles and their adhesive strength are regularly distributed.

Direct study of shungite cement stone structure with the help of scanning election microscope proved that

Table 1

Compound of heavy concrete

No. of compound	Component content					
	cement	sand	rock debris	shungite powder	water	
1	400	720	920	0	160	
2	400	720	920	5	160	
3	400	720	920	10	168	
4	400	720	920	15	192	
5	400	720	920	20	204	

Table 2

Strength of concrete in 28 days of hardening under normal humidity conditions

No. of compound	amount of shungite, %	Ultimate compressive strength, MPa			
		addition of dry shungite	addition of shungite with tempering water		
1	0	32.9	33.1		
2	5	33.5	32.9		
3	10	29.1	29.4		
4	15	28.8	29.0		
5	20	25.6	27.4		

grains of quartz, shungite and portland cement hydration products enveloping them can be seen on the surface of material fracture produced with the usage of shungite powder with specific surface area  $1000 \text{ m}^2/\text{kg}$ . Formation of cement stone structure goes on according to well-known scheme, but it is characterized by deeper cement hydration in case of taken tempering waters amount as well as by greater crystallization of new growths.

Shungite carbon structure peculiarity is that due to accelerated interphase boundary between carbon and



Fig. 3. Strength of concrete in 28 days of hardening under normal humidity conditions

ISSN 2071-2227, Науковий вісник НГУ, 2017, № 3

earth silicon, the main components of shungite rock, these phases form interpenetrating networks. This is the reason why every powder particle of shungite rock contains carbon-bearing and mineral constituent. When quartz is ground, a thin amorphous layer is formed on particle surface. This layer has high chemical activity and prevents aggregation of particles. Aggregation of powder materials during grinding is a significant problem.

It has also been found out that formation of new phase (C–S–H-gel) begins on the surface of shungite grains, furthermore surface of  $C_3S$  particles in the initial period is shielded by hydration products in the least degree in consequence of which the reaction goes on with higher speed.

When shungite is added into portland cement bonding material, the cement stone structure changes in which dispersive weakly crystal low essential calcium silicate hydrates of C-S-H (I) type prevail. They compact the structure and are highly strong and stable to different external impact of the environment.

The least water permeability of cement stone components is featured by cement gel. When shungite is added, the amount of cement gel increases.

Shungite powder was studied for the opportunity to use it as anticorrosive additives and as pigment for producing oil and enamel paints. The studies were carried out according to State Standards 10503-71 "Ready-touse oil paints. Technical conditions" and State Standards 6465-76 "Enamels PF-115. Technical conditions" [7].

According to the research data one of the perspective directions of shungite powder usage can be producing pigment for paint-and-varnish industry.

Structural peculiarities of coatings are defined by physical and chemical interaction of pigment particle surfaces with polymer phase of paint material. Pigment as well as all compounds of paint material performs the basic corrosion-preventing function [8].

It is due to the fact that shungite powder as well as pigments used in paint-and-varnish industry meets the following requirements: high dispersion ability necessary for easier pigments dispersion in film-forming substances. Besides when pigments dispersion increases, their specific impact on paint coat properties increases as well. These properties are as follows: thickening action, films hardening, decrease in permeability, etc. Among the other advantages of shungite powder are low oil absorption; high weather resistance; low density, as pigments with low density are less subjected to formation of dense hardly mixed silt in paints when they are stored; low hardness which makes dispersion easier in film-forming substances; availability and low price of the raw material.

To study anticorrosive properties of varnish-andpaint compounds using shungite concentrates, the samples were prepared by covering glass slides and steel bars with varnish-and-paint compound. To carry out research glass slides of  $90 \times 120$  mm size and 1.3 mm in thickness were used. They were prepared according to State Standards 8832, section 3, and weighted with accuracy to the second decimal sign. Steel bars were prepared for painting by preliminary cleaning of the surface in order to remove sinter, rust and foreign substances before application of varnishand-paint materials. Steel surface was cleaned from rust by a revolvable scratch brush.

Then the surface was polished on a revolving base plate covered with grinding material according to techniques of Rak A. N. [9].

Grinding fineness of shungite powder was defined according to its specific surface area. Specific surface area was defined on the  $\Pi$ CX-10A equipment. Shungite powder with specific surface area of 100 cm<sup>2</sup>/g was obtained for the research. Shungite hardness provides obtaining homogeneous dispersive material on the available equipment, for example, a ball or pearl mill as well as on a vibrating mill.

The compounds of oil and enamel paints with anticorrosion properties on the basis of pigment – shungite powder – were developed. The studied compounds of paints are presented in Table 3.

In order to study impact of shungite powder addition on the properties of varnish-and-paint materials, basic paint compounds characteristics were researched and compared with the standard requirements (covering power, relative viscosity, degree of grinding, and adhesion).

The research results of paint compounds are presented in Tables 4 and 5.

Permanency of paint coatings was studied in relation to proportional action of water. Standard regulates enamel permanency to water no less than 10 hours. As a result of paint compounds testing on the basis of white enamel PF-115 and addition of pigment-shungite powder in ratio stated above – coating permanency to proportional action of water, the following results were obtained (Fig. 5). After painted glass slides being in distilled water for 30 days, control sample No. 1 (white enamel PF-115) completely disrupted paint film adhesion to the surface of glass slide.

Sample No. 2 (grey enamel with shungite pigment 20 %) has fragmentary separation of paint film after 26 days of testing. Paint film of sample No. 3 (dark grey enamel with shungite pigment 40 %) demonstrated good adhesion of glass surface. Consequently, particles of shungite powder reduce film bulking in water, i.e. contribute to developing of protective coatings.

Table 3

Compounds of ready paints

Oil paint	Compounds number and component content according to compositions, mass %				
components	Oil paint		Enamel paint		
	1	2	3	4	
Shungite powder	50	40	20	40	
Oil varnish "Oxol"	50	60	-	—	
White enamel PF-115	_	_	80	60	

### Table 4

		Actual result	
Characteristics	State Standard requirements	Paint compound number	
		1	2
External view of coatings	Surface is even, smooth without separation, micropits, blotchiness, ripples, extraneous impurities, deadish	conforms	
Covering power of dry film, g/cm <sup>2</sup>	No more than 55	55	53,7
Degree of grinding, micrometer	No more than 70	70	70
Relative viscosity, second	65–140	68	67
Coating hardness by the rocker	No more than 0.25	0,25	0,25
Film adhesion, scores,	No more than 2	2	2
Film colour	_	black	black

### Testing results of obtained paints in comparison with State standards 10503-71

### Table 5

Testing results of obtained paints in comparison with State standards 6465-76

		Result	
Characteristic	State standards requirements	Paint compound number	
		3	4
External view of coatings	Surface is even, smooth without separation, micropits, blotchiness, ripples, extraneous impurities, little shagreen is assumed	Deadish, conforms	
Covering power of dry film, g/cm <sup>2</sup>	No more than 90	61	67
Degree of grinding, micrometer	No more than 25	25	25
Relative viscosity, second	60-100	65	68
Coating hardness by the rocker	No less than 0.25	0.25	0.25
Film adhesion, scores	no more than 1	1	1
Film colour	_	grey	dark-grey

In order to study anticorrosive properties of varnishand-paint materials with pigment – shungite powder, steel bars were treated with compounds stated above on the basis of white enamel PF-115.

Painted steel bars (three series) were placed in distilled water, in 3 % solution of NaOH and left in the open air. One bar sample not covered with paint was



Fig. 4. Samples after 30 days of testing for permanency of coating against proportional action of water

placed in distilled water. The state of paint film surface was observed for 3 months. The results of testing are presented in Fig. 5. The studies proved that shungite powder provides anticorrosive protection of steel bars.

#### Conclusion.

The structure of cement stone and concrete was studied. The impact of shungite powder at nanolevel on structure of cement concretes was researched. It was proved that the mechanism of shungite powder impact on cement system is autocatalytic: crystallization of such particles in initial hydrosol at nanolevel automatically leads to further rapid crystallization at microlevel and results in formation of dense structures both in the contact zone and in volume. It provides anticorrosive properties of materials. Electron microscopical studies of cement stone formation through time were carried out in order to justify impact nature of shungite micro- and nano-sized particles on the mechanism of concretes anticorrosive properties formation.

The opportunity to use shungite powder as a pigment and filling material in varnish-and-paint materials was studied. It was proved that shungite powder improved anticorrosive properties of varnish-and-paint materials.



Fig. 5. Steel bars before and after testing in different media

Acknowledgements. The work was sponsored by grants of MES Republic of Kazakhstan 2015-2017 ( $N_{0}$  44-313-2017).

#### References.

**1.** Zhukov, Ye. M., Kropotov, Yu. I. and Luginin, I.A., 2016. Modern methods of concrete structures, buildings and constructions protection from corrosion. *Molodoi uchyony*, 7, pp. 75–78.

**2.** Alekseyenko, A.A., Moskvin, Ye.I. and Ptichnikov, V.A., 2015. Improvement of concrete properties by introduction of active mineral admixture – powdered blast-furnace slag. *Molodoi uchyony*, 24, pp. 80–85.

**3.** L'Hermit, R., 2008. *Idees actuelles sur la technologie du beton*, ISBN 978-5-382-00849-3: 157.

**4.** Wieslaw Kurdowski, 2014. *Cement and Concrete Chemistry*, ISBN: 978-94-007-7944-0.

 Sun, H., Jain, R., Nguyen, K. and Zuckerman, J., 2009. Sialite technology – sustainable alternative to Portland cement. *Clean Technologies and Environmental Policy*, [e-journal] DOI: 10.1007/s10098–009–0258–8.
Palacios, M., Puertas, F., Bowen, P. and Houst, Y. F., 2009. Effect of PCs superplasticizers on the rheological properties and hydration process of slag-blended cement pastes. *Journal o Material Science*, 44(10), pp. 2714–2723. [e-journal] DOI:10.1007/s10853-009-3356.
Yakovlev, A. D., 2008. *Chemistry and technology of paint coatings*. St. Petersburg: KGIMIZDAT. ISBN 978-5-93808-160-4.

**8.** Kalinovskaya, N. N., 2007. Processing properties, strength and effectiveness of concrete, modified by hyperlastificator GP-1. *Stroitel'naya nauka i tekhnika*, 5(14), pp.74–83.

**9.** Rak, A. N., 2007. Structure, processing properties, and design technique fundamentals for composition of selfsealing concrete mixtures. *Stroitel'naya nauka i tekhnika*, 5(14), pp. 52–68.

**Мета.** Поліпшення характеристик міцності й корозійних властивостей бетону на основі дрібнодисперсного вуглецевмісного матеріалу шунгіту.

**Методика.** Польові дослідження в межах рудного поля Бакирчик у Східному Казахстані, відбір проб шунгітових порід для визначення хімічного складу та розподілу основних мінералів і домішок. Для вивчення процесів формування цементного каменю були використані електронно-мікроскопічні дослідження. Були проведені дослідження впливу шунгітових добавок на міцнісні антикорозійні властивості цементного каменю за рахунок впливу шунгітового порошку на його щільність.

Результати. Шунгітові концентрати, отримані з шунгіту Бакирчикського родовища, є перспективними для використання в якості наповнювачів антикорозійного бетону, фарб і лаків. Комплексна розробка золота та шунгітової сировини золотосульфідних родовищ (Бакирчик) відкриває нові економічні перспективи одночасного відпрацювання золота та значні запаси шунгіту, що не використовуються поки, у межах відомих золоторудних полів Східного Казахстану.

Наукова новизна. Було доведено, що шунгітовий порошок в якості пігменту та наповнювача поліпшує антикорозійні властивості лаків і лакофарбових матеріалів.

Практична значимість. Дані розробки дозволять значно скоротити кількість техногенних шунгітовмісних відходів, що нерідко містять забруднюючі речовини та викликають забруднення повітря, грунту й грунтових вод у районах техногенного впливу розробки родовищ золота. Важливість досліджень підтверджується гострою нестачею нових будівельних матеріалів з антикорозійними властивостями. Ці дослідження дозволять створити абсолютно нові матеріали із заданими властивостями для будівельної індустрії Казахстану.

**Ключові слова:** шунгіт, бетон, корозійна стійкість, золотосульфідні родовища

**Цель.** Улучшение прочностных и коррозионных свойств бетона на основе мелкодисперсного углеродсодержащего материала шунгита.

Методика. Полевые исследования в пределах рудного поля Бакырчик в Восточном Казахстане, отбор проб шунгитовых пород для определения химического состава и распределения основных минералов и примесей. Для изучения процессов формирования цементного камня были использованы электронно-микроскопические исследования. Были проведены исследования воздействия шунгитовых добавок на прочностные антикоррозионные свойства цементного камня за счет воздействия шунгитового порошка на его плотность.

Результаты. Шунгитовые концентраты, полученные из шунгита Бакырчикского месторождения, являются перспективными для использования в качестве наполнителей антикоррозионного бетона, красок и лаков. Комплексная разработка золота и шунгитового сырья золотосульфидных месторождений (Бакырчик) открывает новые экономические перспективы одновременной отработки золота и значительные, но не используемые пока запасы шунгита в пределах известных золоторудных полей Восточного Казахстана.

Научная новизна. Было доказано, что шунгитовый порошок в качестве пигмента и заполнителя

UDC [551.72+551.82+551.4.02](477.8)

V. A. Nesterovsky<sup>1</sup>, Dr. Sc. (Geol.), Prof., A. M. Chupryna<sup>1</sup>, M. V. Ruzina<sup>2</sup>, Dr. Sc. (Geol.), Prof., Y. V. Soldatenko<sup>2</sup>, A. El. Albani<sup>3</sup>, Dr. Sc. (Geol.) улучшает антикоррозионные свойства лаков и лакокрасочных материалов.

Практическая значимость. Данные разработки позволят значительно сократить количество техногенных шунгитсодержащих отходов, нередко содержащих загрязняющие вещества, и вызывающие загрязнение воздуха, почвы и грунтовых вод в районах техногенного влияния разработки месторождений золота. Важность исследований подтверждается острой нехваткой новых строительных материалов с антикоррозионными свойствами. Эти исследования позволят создать совершенно новые материалы с заданными свойствами для строительной индустрии Казахстана.

Ключевые слова: *шунгит*, бетон, коррозионная стойкость, золотосульфидные месторождения

*Рекомендовано до публікації О. Н. Кузьміною. Дата надходження рукопису* 23.05.16.

1 – Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

2 – State Higher Education Institution "National Mining University", Dnipro, Ukraine, e-mail: ruzinamarina@rambler.ru 3 – University of Poitiers, Poitiers, France

# STRATIGRAPHIC LEVELS OF VENDIAN (EDIACARAN) BLACK SHALES OF THE TRANSDNIESTRIAN PODILLIA

В.А. Нестеровський<sup>1</sup>, д-р геол. наук, проф., А. М. Чуприна<sup>1</sup>, М. В. Рузіна<sup>2</sup>, д-р геол. наук, проф., Є. В. Солдатенко<sup>2</sup>, А. Єль. Альбані<sup>3</sup>, д-р геол. наук 1 — Київський національний університет імені Т. Г. Шевченка, м. Київ, Україна

2 — Державний вищий навчальний заклад "Національний гірничий університет", м. Дніпро, Україна, e-mail: ruzinamarina@rambler.ru

3 – Університет міста Пуатьє, м. Пуатьє, Франція

## СТРАТИГРАФІЧНІ РІВНІ ЧОРНОСЛАНЦЕВИХ УТВОРЕНЬ ВЕНДУ ПРИДНІСТРОВСЬКОГО ПОДІЛЛЯ

**Purpose.** It is based on investigation of regularities of distribution patterns of black shales in space and time in sections of the Late Proterozoic of the Transdniestria for further investigating by lithological, mineralogical, petrographical and geochemical analysis.

**Methodology.** It consists of field working in outcrops of the Vendian section and their detailed lithological description, facies analysis, petrographical and lithology-geochemical investigations.

**Findings.** A revision of the Late Proterozoic sediment section of the Transdniestrian Podillia was done; conditions of stratification and under- and overburden contacts of layers were updated; textural, structural and other features of stratigraphic layers which indicate genetic and facial aspects of their formation were determined. In the deposits of Mohyliv-Podilskyi range of the Vendian five stratigraphic levels which contain black shale were allocated: lomozivski, liadavski, bronnytski, zinkivski and kaliuski layers. Also new strata of the Ediacaran biota which will be described in detail in the following publications were found.

**Originality.** For the first time, for Mohyliv-Podilskyi range of the Transdniestria five stratigraphic grades of black shale accumulation were distinguished. Black shales precipitated in uncompensated depressions of an epicontinental basin and were concentrated with a lot of organic matter. They could be considered as petroleum source rocks of the Precambrian and Early Paleozoic sedimentary formations of the Volyn-Podillia.

<sup>©</sup> Nesterovsky V.A., Chupryna A.M., Ruzina M.V., Soldatenko Y.V., Albani A. El., 2017