Chem. Chem. Technol., 2024, Vol. 18, No. 1, pp. 7–15

Chemistry

COMPOSITE MATERIALS BASED ON PHOSPHOGYPSUM FOR CONSTRUCTIVE LAYERS OF ROAD PAVEMENT

Yurii Novytskyi¹, Nataliia Topylko^{1,\vee}, Uliana Marushchak², Yura Turba¹

https://doi.org/10.23939/chcht18.01.007

Abstract. The article contains research materials on solving the problem of utilization of waste phosphogypsum by using it in the layers of the road base. For this purpose, composite mixtures based on raw dump phosphogypsum were prepared. The composition of the composite mixtures was optimized to maximize the phosphogypsum content. The phosphogypsum was stabilized with ground granulated blast furnace slag and Portland cement. Laboratory tests have shown that the phosphogypsum-based composite materials meet the requirements of the National Standard of Ukraine DSTU 9177-3:2022 in terms of uniaxial compressive strength and frost resistance. The newly formed mineral phases during the hydration of composite materials based on phosphogypsum-ground granulated blast furnace slag-Portland cement were described using X-ray diffractometric analysis.

Keywords: Phosphogypsum, ground granulated blast furnace slag, Portland cement, composite material, constructive layers of road pavement.

1. Introduction

At the moment, the issue of rational environmental management and reduction of production waste through its utilization is extremely important. Technological waste has a negative impact on human health, the environment and groundwater. The use and recycling of waste is an urgent scientific and applied task, the solution of which will greatly improve the country's environmental safety and will also provide a significant economic effect through the implementation of the principles of the circular economy. At the present stage, Ukraine has not yet managed to bridge the gap between the progressive accumulation of chemical industry waste and measures for its utilization. In particular, the problem of using phosphogypsum, which can be used as a secondary raw material in the construction industry, is not sufficiently

addressed. The safest way to store phosphogypsum is in specially equipped storage facilities that are isolated from water bodies, and the phosphogypsum must be neutralized before being placed in them. However, in Ukraine phosphogypsum is mostly stored only in dumps without special treatment and continues to pollute the environment. The complex of environmental issues related to phosphogypsum dumps is typical for those regions where phosphate mineral fertilizers were or are produced (cities of Sumy, Rivne, Vinnytsia, Kamianske). Improvement of the environmental situation around hazardous facilities with large-tonnage phosphogypsum stockpiles can be achieved through the use of environmentally and economically acceptable disposal processes. However, largetonnage stocks of phosphogypsum are still stored in the dumps of chemical plants. The utilization of phosphogypsum is an important problem not only in Ukraine but in almost all countries of the world. In particular, a significant drawback is the presence of 2-3 % of phosphoric acid and phosphorus compounds in phosphogypsum, which significantly limits its use in construction. Ukraine has already accumulated more than 50 million tons of phosphogypsum. Currently, the average utilization rate of this industrial waste in Ukraine is no more than 2.0 %, although in previous years it reached approximately 2.5 million tons per year (over 10% of current output). The prospect of phosphogypsum processing has faced a complex engineering and economic problem, namely energy consumption and the complexity and multi-stage nature of technological processes for phosphogypsum processing significantly exceed energy consumption in the processing of natural gypsum stone.¹

Phosphate rock was the main raw material for mineral fertilizer production in Ukraine.³⁻⁶ The production of 1 ton of phosphoric acid produces 4.3 to 5.8 tons of phosphogypsum, depending on the type of raw material. As for Ukraine, there are the following producers of phosphoric acid and mineral fertilizers: PJSC Azot (Cherkasy), PJSC DniproAzot and Dnipro Mineral Fertilizer Plant (Kamianske), PJSC RivneAzot (Rivne), CJSC Sumykhimprom (Sumy), Karpatinaftochim (Kalush), and others. Phosphogypsum is mainly stored in dumps at production enterprises and is not used on a large scale due to

¹ Lviv Polytechnic National University, Department of Highways and Bridges. 12 S. Bandery St., 79013, Lviv, Ukraine

² Lviv Polytechnic National University, Department of Building Production. 12 S. Bandery St., 79013, Lviv, Ukraine

 $^{^{}igtarrow}$ nataliia.i.topylko@lpnu.ua

[©] Novytskyi Y., Topylko N., Marushchak U., Turba Y., 2024

the presence of significant amounts of impurities. Phosphogypsum is mostly monomineral, represented by gypsum dihydrate (over 90 %), the rest is acidic phosphorus, sulfur and fluoride residues that remain in the composition of phosphate ore. The diameter of individual phosphogypsum particles ranges from 0.045 mm to 0.250 mm. The moisture content of fresh phosphogypsum is quite high, ranging from 30 to 40%. Long-term storage phosphogypsum is a finely dispersed powder that is prone to clumping with voids forming a loose mass. Freshly formed "wet" phosphogypsum, as opposed to "dry" (longcured) phosphogypsum, is characterized by a low pH (about 2.3-2.8), is considered an acidic by-product, and exhibits high corrosive activity, which is crucial for utilization in the road industry, in particular. The low pH value of fresh phosphogypsum samples may be due to the presence of water-soluble fluorine compounds (possibly H₂SiF₆, Na₂SiF₆, K₂SiF₆, HF), traces of unwashed phosphoric acid and its salts, sulfuric acid, and iron sulfate impurities. It should be noted that phosphogypsum contains heavy metals, which is one of the main problems of phosphogypsum dumps operation. The mobility of heavy metals is related to their ability to hydrolyze. In soils, heavy metals are present in water-soluble, ion-exchange and loosely adsorbed forms. The increased acidity of phosphogypsum creates favorable conditions for the migration of most metals, including heavy metals, which at low pH are in the form of ions or form soluble hydro complexes. In addition, Cu, Cr, Fe (III), Fe (II), Cd, and Pb are capable of forming soluble chlorine-containing complexes, the latter three even in neutral and slightly alkaline - medium. The decrease in acidity in long-term storage phosphogypsum is explained by the gradual leaching or evaporation of acidic compounds from the dumps under the influence of various natural factors. Therefore, it is predicted that long-lasting phosphogypsum will meet the requirements for their use in construction in terms of a set of physical and chemical parameters.

Road construction consumes a significant amount of granular materials and is expected to be one of the most practical and promising ways to valorize phosphogypsum. Recycling of this type of waste can offer modern solutions to the current shortage of construction materials within the circular economy. However, this task is complicated by the impossibility of developing a single technical solution for the management and/or sustainable use of this byproduct due to significant differences in physical and chemical properties, qualitative and quantitative content of impurities, which is a consequence of differences in raw materials, technology, storage conditions and storage life of waste.

In particular, the excess of phosphorus and fluorine compounds over the limit values necessitates chemical treatment of phosphogypsum to convert soluble phosphorus and fluorine compounds into insoluble ones, as well as neutralize residual phosphoric and sulfuric acids, as well as volatile fluorine, which is released into the air during firing. Therefore, a significant number of research papers are aimed at developing and implementing integrated phosphogypsum processing technologies.^{7,8} However, a significant obstacle to the implementation of integrated phosphogypsum processing is the need for long-term energy-intensive preliminary preparation of phosphogypsum, the use of non-standard expensive equipment and special complex technologies. Therefore, despite the existing scientific and technological developments in integrated processing, the number of phosphogypsum dumps is increasing over the years, even in developed countries, and the issue of phosphogypsum waste management is one of the most serious problems.

The composition of long-term storage phosphogypsum in mothballed dumps is mostly close to standard safety standards in terms of radioactivity and the content of harmful impurities. The economic benefits of replacing natural gypsum with phosphogypsum are obvious, and natural resources are saved and significant land areas are unloaded. Of course, technological decisions should be made not only with a view to the economic efficiency of projects, but also in accordance with the requirements of the safety standard system. The resource-efficient use of long-term storage phosphogypsum requires the development of a clear scientific methodology and pilot projects. The history of phosphogypsum use in road construction around the world, presented in papers, ⁹⁻¹⁵ has proven that this valorization method meets specific local needs, conserves raw building materials and does not create a negative impact on the environment.

Thus, road construction using raw dump phosphogypsum is the simplest and most resource-efficient way to utilize it. The use of phosphogypsum in road construction makes it possible to obtain a road pavement structure with improved physical and mechanical properties that meets all existing requirements, as well as to solve the environmental problem by utilizing a multi-ton waste product of mineral fertilizers – phosphogypsum – with minimal fuel and electricity consumption.

A significant number of successful pilot projects have been implemented where raw dump phosphogypsum was used as a stabilizer for structurally unstable soils. Also widely used are the works on the joint stabilization of phosphogypsum with fly ash, lime, metallurgical slag for further use as subgrade, embankment material, and road material.¹⁶⁻¹⁹ According to laboratory tests, such investigated phosphogypsum-based mixtures proved to be environmentally safe and characterized by improved performance.

Given this popularity, the development of technological schemes for the use of phosphogypsum in road construction is a popular issue in the scientific, environmental, and resource-saving fields. The priority issues for the successful use of phosphogypsum are environmental safety, satisfactory road performance, simple and fast technology, and cost-effectiveness.

A laboratory test was conducted to determine the possibility of using composite materials based on raw long-term storage phosphogypsum from the SE "Sirka" of Novyi Rozdil town, in the layers of the road base. The then Rozdil Mining and Chemical Enterprise "Sirka" produced complex mineral fertilizers from 1974 to 1996. The raw materials were Khibinsky apatite concentrate and phosphorite concentrate from Transnistrian deposits in Ukraine.²⁰ After sulfur production ceased, the company ceased operations in 1995 due to lack of raw materials, high energy costs, and non-competitiveness. Instead, the consequences of the production activities of these enterprises remained, in particular, the phosphogypsum dump in the amount of 4.5 million tons. The phosphogypsum dump from Novvi Rozdil covers an area of 14.2 hectares and is surrounded by a 3-meter-high dam.

Based on scientific studies of various binding model systems.²¹ it was decided to form composite mixtures based on phosphogypsum, granulated blast furnace slag and Portland cement. Granulated blast furnace slag consists mainly of a vitreous phase and, according to modern theoretical concepts, is characterized by high internal energy and hydraulic potential. The high internal chemical energy of slag glass ensures its increased solubility, which results in the formation of supersaturated solutions, their crystallization and, as a result, hardening and formation of artificial stone. The mechanism of slag glass hydration is the penetration of negatively charged hydrophilic ions into the glass phase, which disrupts the electrostatic equilibrium of the system and leads to the destruction of the slag structure. Under normal conditions, without activating additives, hydration is prevented by the formation of hydrated silica films on the surface of slag glass particles. The destruction of these films and access to new surfaces of slag grains is facilitated by the introduction of alkaline compounds or sulfates containing Ca^{2+} , (OH)⁻, and (SO₄)²⁻ ions into the aqueous solution. During alkaline activation, hydrated silica is bound into calcium hydrosilicates and calcium hydroalumino silicates. During sulfate activation of slag in the presence of $(SO_4)^{2-}$ ions, needle-shaped crystals of calcium hydrosulfoaluminates are formed in the blast furnace granulated slag-water system, which make it impossible to form waterproof shells on the slag glass phase particles or, in the case of early formation of such shells, destroy them. At the same time, the formation of low-base calcium hydrosilicates is observed, which is accompanied by an increase in strength. It is recommended to add to the sulfate-slag mixture, in addition to gypsum and slag, a small amount of Portland cement clinker for mixed sulfate-alkaline activation of slags.

Taking into account the above, the purpose of the research was formulated, namely designing of composite materials based on phosphogypsum for constructive layers of road pavement.

2. Experimental

2.1. Materials

Long-term storage phosphogypsum from the dump of the SE "Sirka" (Novyi Rozdil, Ukraine) was used to prepare the composite mixtures. The dumps of dry phosphogypsum are erosion-hazardous due to the content of more than 70 % of particles with a diameter of less than 0.14 mm in the surface layer of the dump, which requires the creation of a vegetation cover. Samples of phosphogypsum were taken from different places of the dump under a layer of previously opened soil. The average phosphogypsum sample was then obtained by quarting. The resulting phosphogypsum is a moist, fine powder of light gray color, without a pronounced odor. The phosphogypsum samples were examined for compliance with the requirements of DSTU B V.2.7-2-93 "Building materials. Conditioned phosphogypsum for the production of gypsum binder and artificial gypsum stone. Specifications"²² regarding chemical composition and radioactivity. As can be seen from Table 1, the quality indicators of the used phosphogypsum meet the requirements of the current standard.

The qualitative and quantitative phase composition of phosphogypsum from SE "Sirka" (Novyi Rozdil) and composite materials based on it was studied by X-ray diffractometric analysis. The brand of the diffractometer is DRON ADP-2. Diffractometer operating conditions: I = 12 mA, U = 30 kV, counter speed 2 deg/min. The sensitivity of the method is up to 1 %. The quantitative content of minerals is determined by the Profex program, which is based on the modelling of phase profiles using the JCPDS database, as close as possible to the experimental XRD pattern. The diffractogram of phosphogypsum is shown in Fig. 1.

According to the X-ray diffractometric analysis of phosphogypsum, its main crystalline phase is gypsum dihydrate (89 %), with impurities of up to 11 % in the form of brushite (Br) and ardealite (Ar). The quantitative phase composition of phosphogypsum is shown in Table 2.

The pH of the aqueous extracts of phosphogypsum and soil samples was measured in the laboratory using a pH-150 ionometer. The pH value of individual samples ranged from 5.2 to 5.6. The average pH value for conditioned phosphogypsum from SE "Sirka" is 5.4. Thus, the phosphogypsum produced by SE "Sirka" is characterized by satisfactory performance for further use in road construction.

able 1. Compliance of phosphogypsum of SE Sirka wil	th the requirements of DSTUB V	.2.7-2-93		
	Values of indicators			
and stored in winter, % Mass fraction of phosphate in terms of P ₂ O ₅ , %	Requirements according to DSTU B V.2.7-2-93	Test results		
Calcium sulfate content CaSO ₄ , %	At least 90.00	91.18		
Mass fraction of water in phosphogypsum to be transported and stored in winter, %	No more than 25.00	19.68		
Mass fraction of phosphate in terms of P_2O_5 , %	No more than 1.5	0.378		
Mass fraction of water-soluble phosphates in terms of P_2O_5 , %	No more than 0.15	0.035		
Specific activity of radionuclides, Bq/kg:				
- ²²⁶ Ra		18.8		
- ²³² Th		20.9		
$-{}^{40}$ K		51.6		
Effective specific activity	No more than 370	89.2		
pH	-	5.4		

Table 1. Compliance of phosphogypsum of SE "Sirka" with the requirements of DSTU B V.2.7-2-93

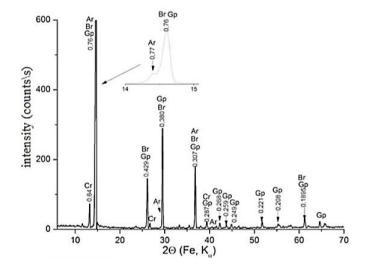


Fig. 1. Diffractogram of phosphogypsum of SE "Sirka". Minerals designation: Gp- gypsum CaSO₄·2H₂O (33-311 JCPDS); Br-Brushite CaPO₃(OH)₄·2H₂O (11-293 JCPDS); Ar-Ardealite CaSO₄(PO₃(OH))₄· 4H₂O (41-585 JCPDS);
Cr- Calcium Aluminum Chromium Oxide Hydrate Ca₄Al₂O₆(CrO₄)₄·9H₂O (42-63 JCPDS)

Table 2. Quantitative phase composition of phosphogypsum of SE "Sirka"

Materials	Mineral	/ chemical formula	Quantity, %	Database JCPDS, №	Notes
	Gypsum	CaSO ₄ ·2H ₂ O	89	33-311	
Long-lasting	Brushite	CaPO ₃ (OH) ₄ · 2H ₂ O	5	11-293	
phosphogypsum with- out drying (in its natu-	Ardealite	CaSO ₄ (PO ₃ (OH)) ₄ · 4H ₂ O	6	41-585	Decomposes after drying
ral state)	Calcium Alumi- num Chromium Oxide Hydrate	Ca ₄ Al ₂ O ₆ (CrO ₄) ₄ ·9H ₂ O	additive	42-63	Unstable com- pound, decom- poses after drying

Table 3. Chemical composition (%) and grinding fineness of granulated blast furnace slag

SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO ₃	grinding fineness by specific surface area, cm ² /g
38.88	6.87	0.80	46.78	4.17	0.69	3380

Granulated blast-furnace slag is used to prepare composite mixtures based on phosphogypsum. The phase composition of the slag is represented by an amorphous glass phase. The oxide composition of granulated blast furnace slag is shown in Table 3. To improve the hydraulic properties of the slag, it was ground to a specific surface area of 3380 cm^2/g . Specific surface area of slag was determined by the Blaine air permeability method.

Portland cement CEM II/A-S 42.5 R, which complies with EN 197-1.2015,²³ was used as a mineral binder in the composition of the composite mixtures.

2.2. Procedure and Methods

CM 3.2

6.15

8.84

The components of the composite mixtures were mixed in a laboratory mixer for 10 minutes in a given ratio until a homogeneous mass was formed. The resulting mixture was pressed at a pressure of 15 MPa, loaded and held for 3 min. The resulting cylinders (d = 5 cm, h = 5cm) were used for further testing. The samples were stored at a temperature of 20 ± 2 °C under conditions of capillary rise of water at a relative humidity of $95 \pm 2\%$ for 28 days, before testing they were completely saturated with water for 48 hours, according to DSTU 8977:2020 (National Standard of Ukraine) Road Materials, Produced by cold recycling technology. Test methods.²⁴

Composite mixtures based on phosphogypsum were investigated for physical and mechanical properties for compliance with the requirements of the State Standard of Ukraine DSTU 9177-3:2022 Crushed stone materials and gravel materials for the road construction industry. Part 3. The Materials bound by the mineral binders.²⁵ To determine the compliance of the composite mixtures with the requirements for reinforced soil according to DSTU 9177-3:2022, the cylinder samples were tested for compressive strength at the age of 7, 28 days and frost resistance. Frost resistance was assessed by the compressive strength after a certain number of freeze-thaw cycles and the frost resistance coefficient.

3. Results and Discussion

In order to maximize the simplification and reduction of technology and accelerate the pace of road construction, it is proposed to study composite mixtures based on raw dump phosphogypsum without preliminary drying and without preliminary mechanical and chemical activation of the components. The composition of the composite mixtures was designed to maximize the phosphogypsum content. The concept of sulfate and alkaline activation of slag was used as the basis for the selection of components for composite mixtures.

Table 4. Composition of composite mixtures based on phosphogypsum from SE "Sirka" and physical parameters of cylinder samples

Symbol for the com-	Content of components in the composite mixture, wt. %			Moisture of the mixture when form-	Average material density,
position of the com- posite mixture (CM)	PG	GGBFS	PC	ing cylinder samples W, %	g/cm ³
CM 1.1	70	25	5	5	1.70
CM 2.1	60	33	7	9	1.75
CM 3.1	55	37	8	9	1.78
CM 3.2	55	35	10	12	1.83

,	Table 5. Physical and mechanical properties of cylinder samples based on composite mixtures									
	Symbol for the composition of	nposition of Compressive strength, MPa, at age, days				The coefficient of softening in water	The coefficient of frost resistance	Grade		
	the composite mixture (CM)	σ_B^7 (C ¹)	σ^{28}_{B} (C ¹)	σ^{28}_{B} (C ²)	σ^{28}_{B} (C ³)	$\sigma^{28}_{\ B}(C^1)\!/\!\sigma^{28}_{\ B}(C^2)$	$\sigma^{28}_{B}(C^3)\!/\!\sigma^{28}_{B}(C^2)$	Giude		
	CM 1.1	2.68	5.55	5.60	2.85	1.01	0.56	M40		
	CM 2.1	3.60	6.45	7.61	5.42	1.18	0.71	M60		
	CM 3.1	5.03	8.16	8.52	5.52	1.04	0.65	M75		

10.37

Notes. C^1 (conditions) – capillary rise of water at a relative humidity of 95±2 %; C^2 (conditions) – curing under conditions of capillary water rise, then complete water saturation for 48 hours before strength testing; C^3 (conditions) – hardening under conditions of capillary rise of water, then complete water saturation within 48 hours, followed by alternating "n" number of freeze-thaw cycles.

97

1.17

0.93

M75

According to 9177-3:2022 for materials with compressive strength: $10MPa \ge \sigma^{28} \ge 7.5MPa$ number of freeze-thaw cycles n=20; $K_{FR} \ge 0.6$; for $\sigma^{28}_B \ge 6.0$ MPa; n=20; $K_{FR} \ge 0.6$; for $\sigma^{28}_B \ge 4$ MPa n=15; $K_{FR} \ge 0.55$

The composite material contains phosphogypsum (PG) from the dump of SE "Sirka" in the amount of 55-70 wt. %, ground granulated blast furnace slag (GGBFS) in the amount of 25-35 wt. % and Portland cement (PC) in the amount of 5-10 wt. %. Table 4 shows the formulation of the composite mixtures and the physical parameters of the cylinder samples. It is shown that the maximum density was obtained for the composite mixture of CM 3.2 at a moisture content of 12 %.

The possibility of using composite mixtures for road pavement layers is determined by physical and mechanical characteristics. The test results of composite mixtures based on phosphogypsum are presented in Table 5. The phosphogypsum-based composite material corresponds to grades M40-M75 in terms of uniaxial compressive strength and frost resistance. The increase in the physical and mechanical properties of the composite mixture CM 3.2 with an increase in the percentage of Portland cement and granulated blast furnace slag is due to the achievement of the maximum density of the material with a decrease in the intergranular space and increased moisture content when forming cylinder samples of 12% compared to the molding moisture content of 5-9% for the rest of the compositions. The increased amount of water ensures the most complete hydration processes with the formation of hydrate phases.

The main disadvantage of gypsum-based materials is insufficient water resistance, which determines a significant decrease in physical and mechanical properties in the event of moisture. The low water resistance of gypsum materials is mainly due to the solubility of gypsum dihydrate, as well as the wedging forces created by water in the pores. Today, there are many ways to increase the water resistance of gypsum, for example, by adding hydraulic binders and/or cheaper mineral additives, but they usually do not provide an increase in water resistance of more than 0.8. Therefore, the field of gypsum application is limited to the narrow limits of operating conditions dry and normal conditions.²⁶ It has been established that composite materials based on phosphogypsum are characterized by high values of the softening coefficient during water absorption; according to Table 5, the values of the softening coefficient for all compositions exceed 1, which makes it possible to classify them as water resistant (with a value of the softening coefficient greater than 0.8 the material is considered water resistant).

To study the peculiarities of the interaction between the components of phosphogypsum-based composite mixtures, their macrostructure and phase composition were investigated after 28 days under conditions of capillary water rise at a relative humidity of 95 ± 2 %. It is shown that composite mixtures with a phosphogypsum content of 55-70 % are characterized by the formation of a heterogeneous macrostructure (Fig. 2).



Fig. 2. Macrostructure of composite materials based on phosphogypsum:1 – phosphogypsum flocs; 2 – cementing matrix

For example, composite materials contain light inclusions 1, represented by phosphogypsum, with a grain size of 0.5-5.0 mm and cementing matrix 2, which predictably corresponds to the composition of a sulfate-slag binder. Such sulphate-slag cements are produced by the joint fine grinding of blast-furnace granulated slag and a sulphate hardening activator (gypsum or anhydrite) with a small addition of an alkaline activator (lime, Portland cement, or burnt dolomite).²¹

The presence of phosphogypsum grains is due to the preparation of composite mixtures using a fast, lowcost technology without long-term mechanical activation of the components. The absence of a stage of joint grinding of the components of the mixture with the simultaneous tendency of raw dump phosphogypsum to clump with the formation of flocs leads to the formation of a heterogeneous macrostructure in which phosphogypsum grains are wrapped in a sulfate-slag hydraulic binder, in which phosphogypsum acts as a sulfate activator.

The phase composition of the sulfate-slag binder component "2" (according to Fig. 2) of composite materials after 28 days of curing was studied using X-ray diffractometric analysis (Fig. 3).

As can be seen from the diffractograms, the mechanism of interaction between the components of the "phosphogypsum-granulated blast furnace slag-Portland cement" systems does not change with an increase in the phosphogypsum content, and the phase composition of the products of the interaction products indicates alkaline-sulfate activation of the slag.²⁷⁻³¹ The phase composition of composite materials (cementitious substance 2) after 28 days is represented by gypsum (d/n= 0.756; 0.429; 0.308;

0.287; 0.268 nm), as well as products of hydration of the components of composite mixtures and interaction between them calcium hydrosilicates (tobermorite (d/n= 1.103; 0.550; 0.308; 0.281 nm), jennite (d/n= 1.050; 0.477; 0.347; 0.329; 0.304; 0.266 nm), ettringite (d/n= 0.973; 0.561; 0.388; 0.348; 0.256 nm) and portlandite (d/n= d/n=0.497; 0.263; 0.193; 0.179 nm)). The formation of hydrosulfoaluminate in the cementitious component due to sulfate activation contributes to the reinforcement of the system at the initial stage of interaction, breaking the gel film on the slag grains, diffusion of SO₄²⁻, Ca²⁺ and OH⁻ ions into the grains and to prolong the hydration reaction and accelerate the strength gain. Analysis of the quantitative phase composition of composite materials composition of composite materials showed that with an increase in the amount of slag and Portland cement the formation of calcium hydrosilicates intensifies. Thus, in the composite material CM3.2, the amount of hydrosilicates is 13 %, while in the composite materials CM1.1 and CM2.1 is 6 % and 10 %, respectively. The increase in the amount of calcium hydrosilicates (CSH-phases), which are decisive in the formation of strength and frost resistance, in the CM 3.1 system occurs both due to the hydration of an increased amount of Portland cement and increased hydraulic activity slag due to its alkaline activation by Ca(OH)₂, a product of Portland cement hydration.

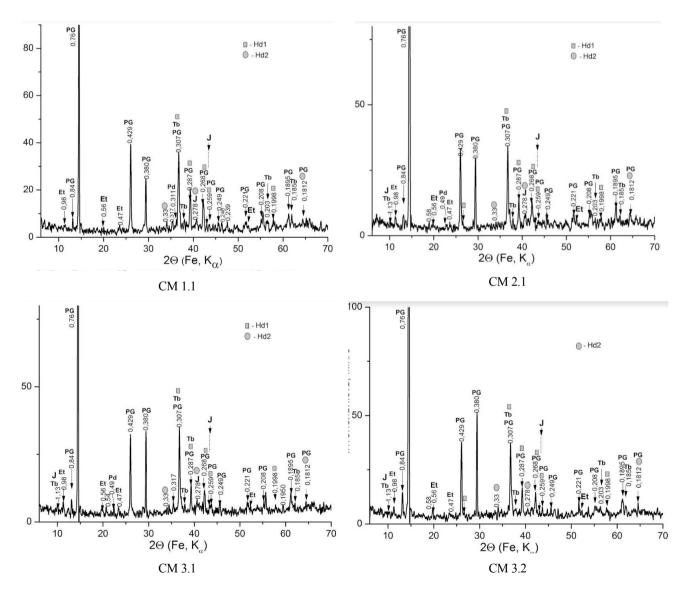


Fig. 3. Diffractograms of sulfate-slag binder component "2" after 28 days of curing: PG – phosphogypsum (gypsum, brushite, ardealite); Et – ettringite; Tb – tobermorytis; Hd₁ – calcium hydrosilicate Ca₂H₂O₅Si; Hd₂ – calcium hydrosilicate Ca₃H₂O_{7,5}Si_{1,5}; Pd – portlandite Ca(OH)₂; J – jenite Ca₉H₂₂O₃₂Si₆

14

4. Conclusions

The possibility of using long-term storage phosphogypsum (SE "Sirka", Novyi Rozdil) for composite mixtures for road pavement layers was established. The results of chemical and radiation analysis indicate that the phosphogypsum used meets the requirements of current Ukrainian standards. It is shown that composite materials based on phosphogypsum, blast furnace granulated slag, and Portland cement after 28 days correspond to the compressive strength and frost resistance of grades M40-M75, and are classified as water-resistant in terms of softening. Using the X-ray diffraction analysis, it was established that the products of hydration and interaction between the components of the composite material based on phosphogypsum are calcium hydrosilicates, ettringite and portlandite. The formation of hydraulically active phases contributes to the acceleration of strength gain, ensures the achievement of water resistance and frost resistance of composite materials based on phosphogypsum.

Abbreviations

PG – phosphogypsum; GGBFS – ground granulated blast furnace slag; PC – Portland cement; CSH – calcium hydrosilicate phase.

References

[1] Ivashchenko, T.; Ince, I. Ecological Aspects of Phosphogypsum Utilization Technologies. Visnyk of Chernihiv State Technological University 2014, 2, 223-228. http://ir.stu.cn.ua/123456789/7462 [2] Chernysh, Ye.Yu.; Vaskin, R.A.; Yakhnenko, O.M. Rozrobka ekolohichno bezpechnykh tekhnolohichnykh rishen utylizatsii fosfohipsu v tekhnolohiiakh zakhystu navkolyshnoho seredovyshcha. Ecological Safety and Balanced Use of Resources 2017, 2, 140–147. https://ebzr.nung.edu.ua/index.php/ebzr/article/view/166 [3] Malanchuk, Z.R.; Korniienko, V.Ya.; Vasylchuk, O.Yu.; Zaiets, V.V. Problemy pererobky ta vyluchennia ridkozemelnykh metaliv z tekhnohennykh rodovyshch fosfohipsu. Science and Education a New Dimension. Natural and Technical Sciences 2018, 179, 55-58. https://doi.org/10.31174/SEND-NT2018-179VI21-14 [4] Malanchuk, Z.; Kornivenko, V.; Malanchuk, Y.; Khrystyuk, A. Results of Experimental Studies of Amber Extraction by Hydromechanical Method in Ukraine. EasternEuropean J. Enterp. Technol. 2016, 3, 24-28 https://doi.org/10.15587/1729-4061.2016.72404 [5] Malanchuk, Z.; Malanchuk, Y.; Kornivenko, V.; Ignatyuk, I. Examining Features of the Process of Heavy Metals Distribution in Technogenic Placers at Hydraulic Mining. EasternEuropean J. Enterp. Technol. 2017, 1, 45-51. https://doi.org/10.15587/1729-4061.2017.92638

[6] Yakhnenko, O.M.; Chernysh, Ye.Yu.; Pliatsuk, L.D.; Trunova, I.O. Samozarostannia vidvalu fosfohipsu yak pokaznyk rivnia tekhnohennoho navantazhennia na dovkillia. *Ecological Safety and Balanced Use of Resources* **2015**, *1*, 110–119.

https://ebzr.nung.edu.ua/index.php/ebzr/article/view/214 [7] Tsioka, M.; Voudrias, E. A. Comparison of Alternative Management Methods for Phosphogypsum Waste Using Life Cycle

Analysis, J. Clean. Prod. 2020, 266, 121386. https://doi.org/10.1016/j.jclepro.2020.121386 [8] Orlovskyy, V.; Bileckyy, V.; Malovanyy, M. Development of Lightweight Grouting Materials Based on By-Products of Ukrainian Industry, Chem. Chem. Technol. 2023, 17, 666-673 https://doi.org/10.23939/chcht17.03.666 [9] Chaimaâ, D.A.; Khaled, L.; Amina, A.; Kamal, E.O. Moroccan Phosphogypsum Use in Road Engineering: Materials and Structure Optimization. J. Mater. Sci. Eng. A. 2022, 12, 115-130. https://doi.org/10.17265/2161-6213/2022.10-12.002 [10] Folek, S.; Walawska, B.; Wilczek, B.; Miśkiewicz, J. Use of Phosphogypsum in Road Construction. Polish J. Chem. Technol. 2011, 13, 18-22. https://doi.org/10.2478/v10026-011-0018-5 [11] Diouri, C.; Echehbani, I.; Lahlou, K.; Omari, K. E.; Alaoui, A. Valorization of Moroccan Phosphogypsum in Road Engineering: Parametric Study. Materials Today: Proceedings 2022, 58, 1054-1058. https://doi.org/10.1016/j.matpr.2022.01.084 [12] Malkawi, D.A.; Rabab'ah, S.R.; AlSyouf, M.M.; Aldeeky, H. Utilizing Expansive Soil Treated with Phosphogypsum and Lime in Pavement Construction. Results in Engineering 2023, 19, 101256. https://doi.org/10.1016/j.rineng.2023.101256 [13] Amrani, M.; Taha, Y.; Kchikach, A.; Benzaazoua, M.; Hakkou, R. Phosphogypsum Recycling: New Horizons for a More Sustainable Road Material Application. J. Build. Eng. 2020, 30, 101267. https://doi.org/10.1016/j.jobe.2020.101267 [14] Meskini, S.; Samdi, A.; Ejjaouani, H.; Remmal, T. Valorization of Phosphogypsum as a Road Material: Stabilizing Effect of Fly Ash and Lime Additives on Strength and Durability. J. Clean. Prod. 2021, 323, 129161. https://doi.org/10.1016/j.jclepro.2021.129161 [15] Zmemla, R.; Benjdidia, M.; Naifar, I.; Sadik, C.; Elleuch, B.; Sdiri, A. A Phosphogypsum-Based Road Material with Enhanced Mechanical Properties for Sustainable Environmental Remediation. Environ. Prog. Sustainable Energy 2022, 41, e13732. https://doi.org/10.1002/ep.13732 [16] Shen, W.; Zhou, M.; Zhao, Q. Study on Lime-Fly Ash-Phosphogypsum Binder. Constr Build Mater. 2007, 21, 1480-1485. https://doi.org/10.1016/j.conbuildmat.2006.07.010 [17] Shen, W.; Zhou, M.; Ma, W.; Hu, J.; Cai, Z. Investigation on the Application of Steel Slag-Fly Ash-Phosphogypsum Solidified Material as Road Base Material. J. Hazard. Mater. 2009, 164, 99-104. https://doi.org/10.1016/j.jhazmat.2008.07.125 [18] Orlovskyy, V.; Malovanyy, M.; Bileckyy, V.; Sokur, M. Physico-Chemical Peculiarities of Weighted Thermostable Plugging Materials Hydration. Chem. Chem. Technol. 2021, 15, 599-607. https://doi.org/10.23939/chcht15.04.599 [19] Orlovskyy, V.; Bileckyy, V.; Malovanyy, M. Research of Lime-Ash Plugging Mixtures. Chem. Chem. Technol. 2022, 16, 621-629. https://doi.org/10.23939/chcht16.04.621 [20] Dzhumelia, E.A. Ekolohichna bezpeka hirnycho-khimichnoho pidpryyemstva na stadii likvidatsii. Ph.D. Thesis [Online]; Lviv Polytechnic National University: Lviv. 2020. https://ena.lpnu.ua/handle/ntb/56155 (accessed Aug 7, 2023). [21] Dvorkin, L.I. Budivelni viazhuchi materialy; Kondor: Rivne, 2019; pp 472-477. [22] DSTU B V. 2.7-2-93 (National Standard of Ukraine) Building materials. Phosphogyps Conditional for the production of gypsum binder and artificial gypsum stones. [23] DSTU B EN 197-1:2015 (National Standard of Ukraine) Cement. Part 1: Composition, specifications and conformity criteria for common cements (EN 197-1:2011, IDT). [24] DSTU 8977:2020 (National Standard of Ukraine) Road Materials, Produced by cold recycling technology. Test methods. [25] DSTU 9177-3:2022 (National Standard of Ukraine) Crushed stone materials and gravel materials for the road building industry. Part 3. The Materials bound by the mineral binders.

[26] Yefimenko, A.S. Pidvyshchennya vodostiikosti hipsu polifraktsiinymi mineralnymy dobavkamy. Ph.D. Thesis, Ukrainian State University of Railway Transport: Kharkiv, 2021.

[27] Ye, H.; Chen, Z.; Huang, L. Mechanism of Sulfate Attack on Alkali-Activated Slag: The Role of Activator Composition. *Cem Concr Res* 2019, *125*, 105868. https://doi.org/10.1016/j.cemconres.2019.105868
[28] Ivashchyshyn, H.; Sanytsky, M.; Kropyvnytska, T.; Rusyn, B. Study of Low-Emission Multi-Component Cements with a High Content of Supplementary Cementitious Materials. *EasternEuropean J. Enterp. Technol.* 2019, *4*, 39–47. https://doi.org/10.15587/1729-4061.2019.175472

[29] Krivenko, P.; Sanytsky M.; Kropyvnytska T. Alkali-Sulfate Activated Blended Porland Cements. *Solid State Phenom.* **2018**, *276*, 9–14. https://doi.org/10.4028/www.scientific.net/SSP.276.9

[30] Marushchak, U.; Sanytsky, M.; Pozniak, O.; Mazurak, O. Peculiarities of Nanomodified Portland Systems Structure Formation. *Chem. Chem. Technol.* 2019, 13, 510–517

https://doi.org/10.23939/chcht13.04.510

[31] Solodkyy, S.J.; Novytskyi, Y.L.; Topylko, N.I.; Turba, Y.V. Research of Influence of Polymer Additives-Stabilizers on Physical-Mechanical Indicators and Microstructure of Cement Ground. *IOP Conf. Ser.: Mater. Sci. Eng.* **2019**, *708*, 012107. https://doi.org/10.1088/1757-899X/708/1/012107

КОМПОЗИЦІЙНІ МАТЕРІАЛИ НА ОСНОВІ ФОСФОГІПСУ ДЛЯ КОНСТРУКТИВНИХ ШАРІВ ДОРОЖНЬОГО ОДЯГУ

Анотація. Стаття містить матеріали досліджень щодо вирішення проблеми утилізації відходів фосфогіпсу через його використання в шарах основи дорожньої конструкції. З цією метою були приготовані композиційні суміші на основі сирого відвального фосфогіпсу. Склад композиційних сумішей оптимізовано таким чином, щоб вміст фосфогіпсу був максимальним. Фосфогіпс стабілізували доменним гранульованим шлаком і портландцементом. Лабораторними випробуваннями встановлено, що композиційні матеріали на основі фосфогіпсу задовольняють вимоги ДСТУ 9177-3:2022 Частина 3, Матеріали укріплені мінеральними в'яжучими, за показниками міцності на одноосьовий стиск і морозостійкості. Х-променевим дифрактометричним аналізом виявлено новоутворені мінеральні фази в процесі гідратації композиційних матеріалів на основі "фосфогіпсдоменний гранульований шлак-портландцемент".

Received: October 20, 2023 / Revised: December 29, 2023 / Accepted: January 15, 2024 Ключові слова: фосфогіпс, мелений гранульований доменний шлак, портландцемент, композитні матеріали, основа дорожнього покриття.