Vol. 8, No. 4, 2023

VALORIZATION OF PHOSPHOGYPSUM IN UKRAINE BY CREATING COMPOSITE MATERIALS FOR STRUCTURAL LAYERS OF ROAD PAVEMENT

Yurii Novytskyi, Nataliia Topylko, Nataliia Rainchuk

Department of Highways and Bridges,
Lviv Polytechnic National University,
12, S. Bandery Str., Lviv, 79013,Ukraine
nataliia.i.topylkoi@lpnu.ua

https://doi.org/10.23939/ep2023.04.247

Received: 30.10.2023

Abstract. Ukraine's transition to an energy-efficient economy as part of its overall transformation to EU standards is a difficult but crucial challenge. The country's post-war recovery will involve modernizing the entire infrastructure in line with EU sustainable development standards. In particular, the road sector, being the most resource-intensive in construction, must be in line with the goals of the European Green Deal, namely: reducing greenhouse gas emissions resulting from the extraction and processing of natural resources, implementing the principles of the circular economy, achieving economic growth by maximizing the substitution of natural materials for man-made waste, minimizing negative environmental impact and using advanced green technologies (Natsionalna ekonomichna stratehiia, 2021).

Promoting the principles of the circular economy and implementing the best European practices in the reuse of industrial waste is not only a requirement for Ukraine's successful accession to the EU, but also a prerequisite for the effective implementation of infrastructure projects, especially during the post-war reconstruction of the country. However, such ambitious goals can be a huge challenge for our country, particularly in environmental recycling projects in construction, where the most important issue is to eliminate the simplest and most attractive solution of using natural materials rather than replacing them with industrial waste.

The article contains research materials on solving the problem of utilization of phosphogypsum waste by using it in the structural layers of road pavements. For this purpose, composite mixtures based on raw dump phosphogypsum (SE “Sirka”, Novyi Rozdil) were prepared. Laboratory tests have established that composite materials based on phosphogypsum meet the requirements of the State Standard of Ukraine for structural layers of road pavement.

Keywords: circular economy, European Green Deal, road construction, phosphogypsum, composite materials.

1. Introduction

The global circular economy, which is a certain concept of economic development based on a closed cycle, is capable of reducing the use of natural resources by 30 %, bringing human activity back within the safe limits of the planet. Every year, due to the growth of resource extraction and use, the situation in the world is deteriorating (Kondratenko, Shylovtseva, 2023). Unfortunately, there is a disappointing trend in the circularity of economic activity – from 9.1 % in 2018, to 8.6 % in 2020, and to 7.2 % in 2023. This indicates that more than 90 % of resources are consumed or remain unavailable for reuse for many years. To return economic activity to safe limits, it is advisable to reduce global resource production and consumption by one third.

At the present stage, Ukraine has not yet managed to bridge the gap between the progressive accumulation of man-made chemical waste and measures for its utilization. In particular, the issue of phosphogypsum utilization is quite problematic. The use of phosphogypsum is an important problem not only in Ukraine but in almost all countries of the world. The presence of 2–3 % residual phosphoric acid and phosphorus compounds in phosphogypsum limits its use in both agriculture and construction. For example, only about 6 % of its total amount is used in agriculture as a fertilizer containing phosphorus. Currently, the

For citation: Novytskyi, Y., Topylko, N., Rainchuk, N. (2023). Valorization of phosphogypsum in Ukraine by creating composite materials for structural layers of road pavement. *Journal Environmental Problems*, *8*(4), 247–255. DOI: https://doi.org/10.23939/ep2023.04.247

average utilization rate of this industrial waste in Ukraine is no more than 2.0 %, although in previous years it reached about 2.5 million tons per year (over 10 % of current output). Current global reserves of phosphogypsum are estimated at around 100–280 million tons per year (Ivashchenko, 2016; Tayibi, 2009). The mass share of its utilization, according to the most optimistic forecasts, does not exceed 10–15 %. Ukraine has already accumulated more than 50 million tons of phosphogypsum. A set of environmental issues related to their management is typical for those regions where phosphate mineral fertilizers were or are produced (Sumy, Rivne, Vinnytsia, Kamianske). In particular, phosphogypsum reserves in the dump of the Dnipro Mineral Fertilizer Plant (Kamianske) amount to almost 15 million tons. Sumy region has already accumulated more than 14 million tons of this waste. 700,000 tons of phosphogypsum have been "decorating" Vinnytsia Oblast for more than 20 years, since the chemical plant went bankrupt. The production activities of the Sirka Mining and Chemical Enterprise (Novyi Rozdil), which went bankrupt in 1995, resulted in a 4.5 million-ton phosphogypsum dump (Malanchuk et. al., 2016; Yakhnenko et. al., 2015; Chernysh et. al., 2021).

The safest way to store phosphogypsum is in specially equipped storage facilities that are isolated from water bodies as much as possible. Phosphogypsum must be neutralized before it is stored. A significant problem is that in Ukraine, phosphogypsum is stored only in dumps without special treatment and continues to pollute the environment. At the same time, the use of gypsum materials in construction is increasing, and the limited number of gypsum stone deposits exacerbates the problem of finding sources of conditioned gypsum raw materials. At the same time, the problem of using phosphogypsum, large-tonnage reserves of which are stored in the dumps of chemical plants, which can be used as raw materials in the construction industry, is not being solved. The prospect of phosphogypsum processing faces a complex engineering and economic problem. The energy consumption for phosphogypsum processing is significantly higher than that of natural gypsum stone (Ivashchenko, 2016).

The problem described above has shaped the task of solving it, namely finding innovative methods of phosphogypsum utilization that support the principles of the circular economy and green technologies.

2. Theoretical part

In Ukraine, the largest amount of gypsum-containing industrial waste is produced from phosphogypsum. Phosphogypsum is a product of sulfuric acid processing of apatite or phosphorite into phosphoric acid or concentrated phosphate fertilizers (Dvorkin, 2019). When natural phosphates are decomposed by sulfuric acid, phosphoric acid is dissolved into solution and hardly soluble calcium sulfate is formed. In general, the reaction of apatite with a mixture of sulfuric and phosphoric acids is as follows:

$$Ca_5(PO_4)_3F+5H_2SO_4+nH_3PO_4+$$
$$+ mH_2O=(n+3)H_3PO_4+5CaSO_4+mH_2O+HF$$

The crystalline precipitate of calcium sulfate is separated from the phosphoric acid by filtration. 1 ton of extraction phosphoric acid (in terms of 100 % H_3PO_4) produces 3.6–6.2 tons of phosphogypsum in terms of dry matter. At some enterprises, the annual output of phosphogypsum reaches 2.5 million tons. The cost of transportation and storage in dumps accounts for 30% of the total cost of construction and operation of the main production.

The chemical composition of phosphogypsum mainly depends on the quality of the raw phosphate rock and the method of production of extraction phosphoric acid. In Ukraine, Kolsky's apatite concentrate was mainly used as a phosphate rock (Dvorkin et. al., 2009). The generalized chemical composition of Ukrainian phosphogypsum is presented below (in %): CaO=39–40; SO_3=56–57; P_2O_5(total content)= 1.0–1.2; P_2O_5(water-soluble) = 0.5–0.6; F=0.3–0.4. The presence of impurities complicates the use of phosphogypsum, and in some cases it becomes impossible. For example, in the case of high radioactivity or excessive heavy metal content. The radioactivity of phosphogypsum based on Kolsky apatite, which is widely used in Ukraine, is within normal limits. Extraction phosphoric acid is produced using dihydrate and semi-hydrate methods. Depending on the temperature and concentration of the phosphoric acid produced, calcium sulfate can be separated into gypsum dihydrate $CaSO_4 \times 2H_2O$, gypsum semihydrate $CaSO_4 \times 1.5H_2O$, and anhydrite $CaSO_4$.

In the wet method of producing phosphate fertilizers, phosphogypsum mainly consists of gypsum bicarbonate (93–95 %) with a mechanical admixture of 1–1.5 % P_2O_5 and some silica and other oxides (Tsioka, 2020). At the same time, phosphogypsum looks like a slurry with a moisture content of about 40 %. The solid phase of the slurry is finely dispersed and consists of more than 50 % of particles smaller than 10 microns. The gypsum dihydrate in phosphogypsum is in the form of needle-like crystals and growths. In the production of phosphoric acid by the extraction method, the by-product is phosphogypsum with a moisture content of up to 25 %, containing 92–95 % α-$CaSO_4 \times 0.5H_2O$, i.e. the main component of high-strength gypsum. However, the presence of passivating films on the surface of the semihydrate crystals reduces the ability of this product to exhibit binding properties.

Thus, phosphogypsum contains 80 to 98 % of gypsum of various modifications and can be confidently classified as gypsum raw material. The high dispersion of phosphogypsum (grinding fineness by specific surface area 3500–3800 cm^2/g) makes it possible to exclude the grinding stage from the processing process. At the same time, the high moisture content of phosphogypsum complicates its transportation and leads to fuel overconsumption during drying. The presence of water-soluble, especially phosphorus and fluorine-containing impurities in phosphogypsum complicates the production of gypsum binders from it and involves washing and neutralization processes, which leads to high heat consumption, complexity and multi-stage technology. But the most important thing is that gypsum binders produced using conventional phosphogypsum processing technology are of low quality. The negative impact of impurities on the construction qualities of phosphogypsum can be partially reduced by additional grinding and forming products using vibratory laying. In this case, the quality of the phosphogypsum binder is slightly improved, although it remains lower than that of natural gypsum.

The main methods of phosphogypsum preparation in the production of gypsum binders can be divided into four groups (Dvorkin, et. al., 2009):

– rinsing phosphogypsum with water;

– rinsing combined with neutralization and precipitation of impurities in an aqueous suspension;

– method of thermal decomposition of impurities;

– introduction of neutralizing, mineralizing, crystallization regulating additives before and after the firing stage.

These methods of the first and second groups are accompanied by the generation of a significant amount of contaminated water (2–5 m^3 per 1 ton of phosphogypsum) and additional costs for wastewater treatment. Methods of the third and fourth groups are not widely used. In particular, the implementation of the fourth method requires the use of scarce additives that do not fully ensure the stability of the properties of phosphogypsum-based binders.

It has been pointed out (Tayibi, 2009; Cao, 2022) that in the world, phosphogypsum (up to 15 %) is mainly utilized in the manufacture of construction materials, as a soil amendment and as a hardness regulator in the production of Portland cement. However, this use is prohibited in most countries. The reason for the ban is the excessive content of radionuclides and heavy metals. However, before making a decision on phosphogypsum utilization, you should carefully study the norms of the state standard on the content of harmful substances. It is clear that the concentration of impurities that limit the use of phosphogypsum will not be stable and will be determined by the origin of raw materials, the technology of phosphate fertilizers production, and the conditions of storage of technogenic waste in the dump. Therefore, each phosphogypsum dump will have its own "unique" composition and will require a specific utilization technology.

Freshly formed "wet" phosphogypsum, as opposed to "dry" phosphogypsum (long term aging), 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 construction industry, in particular. The low pH value of fresh phosphogypsum samples may be due to the presence of water-soluble fluorine compounds (possibly H_2SiF_6, Na_2SiF_6, K_2SiF_6, HF), traces of unwashed phosphoric acid and its salts, and sulfuric acid. Long-lasting phosphogypsum is a finely dispersed powder that is prone to clumping and voids forming a loose mass. The decrease in acidity in long-lasting phosphogypsum is explained by the gradual leaching or evaporation of acidic compounds from the dumps under the influence of various natural factors (Wu, 2022; Cánovas, 2018). Thus, 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. A simplified accelerated technology can be used to produce gypsum binders from long-lasting phosphogypsum. Mixing long-life dump phosphogypsum with 1–3 % quicklime results in almost complete neutralization of residual acidic impurities.

A significant number of scientific studies and pilot projects are aimed at using raw phosphogypsum (without prior neutralization, drying and firing) in the structural layers of road pavement. The use of phosphogypsum in road construction, compared to ash and slag and/or blast furnace slag, is not widely used. However, 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. When constructing a highway, more than 50 % of its cost is the cost of materials. To build 1 km of road, depending on its category and local conditions, from 6 to 60 thousand m^3 of soil is required for the construction of the subgrade; 1.5–6.0 thousand m^3 of sand for the drainage and frost protection layer; 0.8–5.4 thousand m^3 of crushed stone or soil reinforced with binders. Reducing the need for these materials, especially the most expensive and scarce ones, and increasing the efficiency of their use is one of the most pressing problems on which scientific and technological progress in the road industry depends (Mozghovyi, 2014; Acıkök, 2018; Smith, 2007, Abdullah, 2021; Arm, 2003).

The cementitious substance, obtained on the basis of raw phosphogypsum in the form of gypsum bicarbonate, is placed in the structural layers of the pavement in the form of dry mixtures with minerals (sand, cement, silica, fly ash, ash and slag, blast furnace granulated slag, metallurgical slag) and pre-compacted to a density of 1.8–2.0 g/cm^3, according to standard road construction technology (Dvorkin, et. al, 2009). Only then is it treated with water in the amount required for the hydration process. The use of rigid mixtures with a compaction stage leads to an increase in the strength and water resistance of phosphogypsum compositions by 2–3 times compared to similar indicators for phosphogypsum compositions produced by the bulk method. Compaction makes it possible to realize the possible activity of the composite binder and compensate for the negative impact of impurities.

The positive results of using phosphogypsum in road construction are evidenced by a number of pilot projects that highlight global experience (Phosphogypsum: Sustainable Management and Use, 2016). The most well-known foreign road construction projects using phosphogypsum are:

– the United States of America was the first to implement large-scale phosphogypsum utilization projects in road construction since 1985. Initially, phosphogypsum was mainly used to stabilize structurally unstable soils. Improving the performance of the subgrade underlying the road structure led to further research in this area;

– construction of a roadway in rural areas in 1999 in Maaninka (Finland). The large-scale study was aimed at reconstructing a rural road that required annual repairs in the winter and spring... The test road consisted of two sections, each about 1.7 km long. Laboratory tests showed that the mixture of phosphogypsum and fly ash performed better in freezing/thawing conditions than traditional materials. Laboratory tests of the materials themselves, as well as further tests of the construction materials at the pilot sites, proved that the phosphogypsum and fly ash mixtures meet the environmental acceptance criteria of EU regulations;

– the experience of building an internal road at the Jordan Phosphate Mines Company (JPMC) in Jordan is quite interesting. The road was built to provide access to a drilling mud stack located just behind the chemical shop. The construction technology was extremely simple and consisted only of building a bed of bulk unprocessed phosphogypsum. After 20–30 years of heavy vehicles driving over the surface of the phosphogypsum, compacting it with pozzolanic properties without adding cement and forming a hard, high-strength crust on the surface.

– the first experimental pilot project of a one-kilometer-long road was built in Safa (Morocco) in 2017 (Chaimaâ, 2022). Four different material compositions based on phosphogypsum with cement addition provided high mechanical strength and durability compared to traditional materials. The environmental impact was found to be safe.

Unfortunately, the experience of phosphogypsum road construction in Ukraine is not widespread. Insufficient attention has been paid to the development of rational ways to use phosphogypsum composite materials in the current economic conditions for road construction in Ukraine. Therefore, there is a need to implement and improve the foreign experience of using phosphogypsum in road structures in accordance with national standards and practical ways of implementation.

Thus, road construction is an important area that will increase the level of phosphogypsum utilization in Ukraine. This is a very promising area, as the country will implement large-scale road rehabilitation projects.

3. Materials and Methods

Materials. For the preparation of composite materials, phosphogypsum was used from the preserved dump of SE “Sirka” (Novyi Rozdil). The elemental composition of phosphogypsum from SE “Sira” was studied using an ElvaX Light SDD spectrometer from Elvatech. The test data are shown in Table 1.

For the sample of phosphogypsum from SE “Sirka”, tests for the qualitative phase composition were carried out (Fig. 1) using X-ray diffractometric analysis. The operating conditions of the diffractometer are as follows: I = 12 mA, U = 30 kV, meter speed 2 deg/min. The sensitivity of the method is up to 1 %. The quantitative content of minerals was determined using the Profex program, which is based on modeling phase profiles using the JCPDS database, which are as close as possible to the experimental X-ray structure. According to the X-ray diffractometric analysis of phosphogypsum, its main crystalline phase is dilute gypsum (89 %), with impurities of up to 11 % in the form of brushite (Br) and ardealite (Ar).

Table 1

Elemental composition of phosphogypsum at SE "Sirka" (Novyi Rozdil)

The atomic number	The Element	The Series	The Intensity	The Concentration
15	P	K	0	< 0.068 %
16	S	K	1101712	7.195 ± 0.039 %
20	Ca	K	101973	58.249 ± 0.138 %
22	Ti	K	1038	0.741 ± 0.116 %
26	Fe	K	5056	0.553 ± 0.022 %
37	Rb	K	1831	0.012 ± 0.003 %
38	Sr	K	1130425	6.427 ± 0.034 %
39	Y	K	6987	0.035 ± 0.003 %
40	Zr	K	13181	0.061 ± 0.007 %
58	Ce	L	1520	1.248 ± 0.147 %
74	W	L	0	< 0.006 %

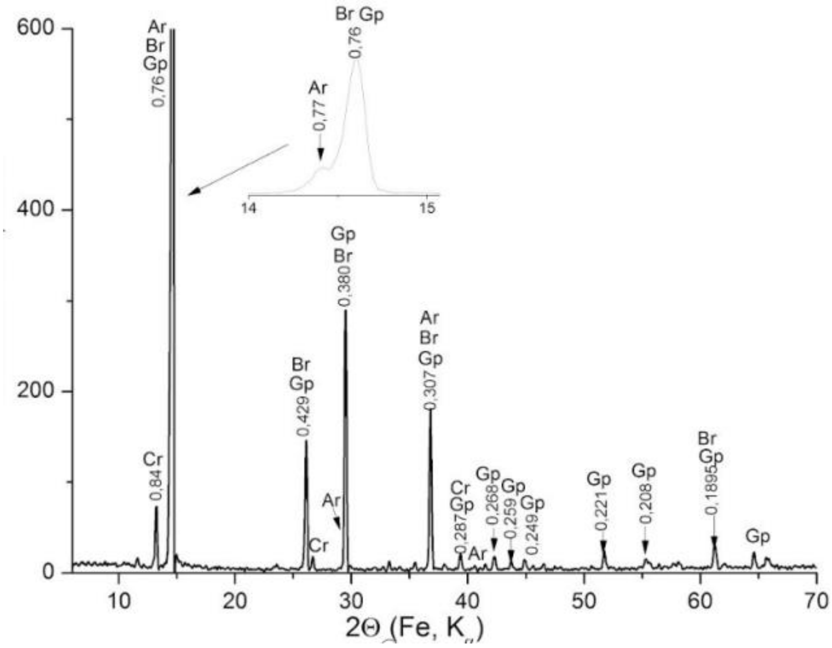

Fig. 1. Diffractogram of phosphogypsum of SE "Sirka". Minerals designation: Gp- gypsum $CaSO_4{\cdot}2H_2O$ (33-311 JCPDS); Br-Brushite $CaPO_3(OH)_4{\cdot}2H_2O$ (11-293 JCPDS); Ar-Ardealite $CaSO_4(PO_3(OH))_4{\cdot}4H_2O$ (41-585 JCPDS); Cr- Calcium Aluminum Chromium Oxide Hydrate $Ca_4Al_2O_6(CrO_4)_4{\cdot}9H_2O$ (42-63 JCPDS)

In appearance, phosphogypsum is a moist, fine white crystalline powder. The particle size of phosphogypsum does not exceed 0.2 mm. The results of phosphogypsum analysis in accordance 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" on chemical composition and radioactivity are presented in Table 2 (National Standard of Ukraine DSTU B V. 2.7-2-93).

Table 2

Conformity of phosphogypsum of SE "Sirka" to the requirements of the national standard

Designation	Component content, wt.%.						Effective specific activity of radionuclides, Bq/kg
	$CaSO_4 \times 2H_2O$	Phosphates		Fluorides (F)		Moisture content (in winter)	
Standard requirements	90	total P_2O_5	watersoluble P_2O_5	total	watersoluble		
		1.5	0.15	0.40	0.30	25	370
phospho gypsum	91.18	0.378	0.035	–	–	19.68	89.2

The pH of the aqueous extracts of the phosphogypsum sample was measured in the laboratory using a PX-150 ionometer. The pH value for the dump phosphogypsum of SE "Sira" is 5.4. Thus, the phosphogypsum produced by SE "Sirka" is characterized by satisfactory indicators for further use in road construction.

For the preparation of composite materials based on phosphogypsum, granulated blast furnace slag was additionally introduced. The phase composition of the slag is represented by an amorphous glass phase. To improve the hydraulic properties of the slag, it was ground to a specific surface area of 3380 cm^2/g. Portland cement CEM II/A-S 42.5 R, which complies with EN 197-1:2015, was used as a mineral binder in the composite mixtures.

General methods. The components of the composite mixtures were mixed in a laboratory mixer bowl in a given ratio for 10 minutes 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=5 cm) were used for further tests. The samples were stored at a temperature of 20 ± 2 °C under conditions of capillary water rise at a relative humidity of 95 ± 2 % for 28 days, before testing they were completely saturated with water for 48 hours according to the National Standard of Ukraine (DSTU 8977:2020).

The phosphogypsum-based composite materials were investigated for compliance with the requirements of the National Standard of Ukraine 9177-3:2022 Crushed stone materials and gravel materials for the road building industry. Part 3. The Materials bound by the mineral binders (DSTU 9177-3:2022). To determine the compliance of the composite materials with physical and mechanical properties, we tested the cylinder specimens for compressive strength at the age of 7 and 28 days and frost resistance. Frost resistance was evaluated by the compressive strength after a certain number of freeze-thaw cycles and the frost resistance coefficient.

4. Results and Discussion

In the development of composite materials for the structural layers of the road pavement, we used the technogenic waste available in Ukraine: phosphogypsum, ground blast-furnace slag. Portland cement was used as a mineral binder. When planning the experiment, it was proposed to use the concept of sulfate-alkaline activation of slags. It is predictable that in the absence of a technological stage of long-term compatible mechanical activation of components, the macrostructure of the composite material will be heterogeneous. That is, raw dumped phosphogypsum, which is prone to clumping and poorly mixed, will be randomly placed in the medium of the composite material with the formation of flocs. At the same time, these phosphogypsum flocs will be wrapped in a sulfate-slag hydraulic binder, which will serve as a reinforcing waterproof material.

Sulphate-slag cements are produced by the joint fine grinding of blast-furnace granulated slag and a sulphate curing agent (gypsum) with a small addition of an alkaline activator (mainly Portland cement up to 10%) (Dvorkin, 2019). An alkaline environment is important for the normal curing of sulfate-slag binders. The content of blast furnace slag in the composite material will increase corrosion resistance. Ground blast-furnace granulated slag is a product formed by the rapid cooling of molten slag solution obtained in a blast furnace during the iron ore smelting process. The chemical composition of blast furnace slag is similar to that of Portland cement and contains mainly three oxides – calcium, silicon and aluminum – which have already formed the germs of Portland cement clinker minerals. As a result, it actively exhibits binding properties by interacting with the hydration products of cement clinker minerals and gypsum.

Taking into account the principles of sulfate-alkaline activation of slag, it was proposed to prepare a test mixture for a composite material that would serve as a structural layer of pavement. The composition of the composite mixture was designed to maximize the phosphogypsum content. The composite material, based on phosphogypsum from the dump of SE “Sirka” (PG) in the amount of 50 wt.%, ground granulated blast furnace slag (GGBFS) in the amount of 43 wt.% and Portland cement (PC) in the amount of 7 wt.%, is characterized by the following physical and chemical parameters, which are presented in Table 3.

Table 3

Physical – mechanical properties of the composite material based on the mixture PG-GGBFS-PC

Pressure of the press, P (MPA)	Moisture content of the mixture when pressing cylinder samples W (%)	Density of sample cylinders ρ (g/cm^3)	Compressive strength (MPa), at age (days)				The coefficient of softening in water K_{soft} $^2R_{st(28)}/^1R_{st(28)}$
			$^1R_{st(7)}$	$^1R_{st(28)}$	$^2R_{st(28)}$	$^3R_{st(28)}$	
15	9	1.83	2.08	4.85	5.05	1.98	1.04
	12	1.88	3.46	6.55	7.16	5.82	1.09
	16	1.95	5.43	8.16	9.92	7.92	1.21
	18	1.98	7.01	8.84	11.53	10.37	1.30

Note:

Storage conditions of cylinder samples for determining compressive strength $^nR_{st}$:

1 – strength under conditions of capillary rise of water at relative humidity 95±2 %;

2 – strength under conditions of capillary water rise, followed by full water saturation for 48 hours before strength testing;

3 – strength under conditions of capillary rise of water, then complete water saturation within 48 hours with the subsequent alternation of a certain number of freezing-thawing cycles “n” according to DSTU 9177-3:2022

The degree of compaction of the mixture significantly affects the processes of phase and structure formation in the composite material. With an increase in the degree of density, porosity decreases, water and frost resistance, mechanical strength, and ultimately the durability of the material increases. With maximum compaction of the mixture, excess air is displaced from its volume, the liquid phase and solid particles of the components are redistributed, resulting in a denser package, and the number and area of contacts between grains increases. To improve the compaction processes, ensure the workability of the mixture, and increase the completeness of the hydration processes of cementitious substances, it is necessary to increase the water content. According to laboratory tests (shown in Table 3), at the highest moisture content of 18 %, the composite material is characterized by the highest numerical values of the compressive strength.

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 its solubility, as well as the wedging forces created by water in the pores (Yefimenko, 2021). Therefore, the field of application of gypsum is limited by the narrow boundaries of operating conditions - dry and normal conditions. 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 3, the values of the softening coefficient of the composite material for all degrees of humidity exceed 1, which makes it possible to classify them as water-resistant (with a value of the softening coefficient of more than 0.8, the material is considered water-resistant and is obviously provided by the formation of sulfate-slag hydraulic cement.

The possibility of using a phosphogypsum-based composite material for structural layers of pavement is determined by compliance with the requirements of National Standard 9177-3:2022. The results of compliance with the requirements of the standard are presented in Table 4.

Table 4

Conformity of the composite material based on phosphogypsum of SE "Sirka" to the requirements of the national standard

Designation	Physical and mechanical properties			Compliance to the strength grade
	Compressive strength $^{2}R_{st(28)}$, (MPa)	Number of freeze-thaw cycles "n"	The coefficient of frost resistance K_{fr} $^{3}R_{ст(28)}/^{2}R_{ст(28)}$	
Standard requirements for physical and mechanical parameters	≥ 1	Not standardized		M10
	≥ 2	10	≥ 0.50	M20
	≥ 4	15	≥ 0.55	M40
	≥ 6	20	≥ 0.60	M60
	$10 \geq R^{28}_{st} \geq 7.5$	20	≥ 0.60	M75
Composite material W=9%	5.05	9	0.39	M10
Composite material W=12%	7.16	20	0.81	M60
Composite material W=16%	9.92	20	0.80	M75

The composite material at an initial moisture content of 9 % does not meet the expected M40 grade in terms of physical and mechanical properties. Obviously, insufficient moisture content of the material during the formation of cylinder specimens prevents the formation of hydrated cement phases, which are actually responsible for the increase in strength and frost resistance. With increasing moisture content, the composite material undergoes hydration processes with the formation of new phases inherent in sulfate-slag hydraulic cement, namely calcium hydrosilicates (CSH phases) and ettringite (Marushchak, 2019). The formation of ettringite in the cementitious component due to sulfate activation of slag contributes to the reinforcement of the system at the initial stage of interaction, the rupture of the gel film on the slag grains, the diffusion of $(SO_4)^{2-}$, Ca^{2+} and $(OH)^{-}$ ions into the grains and the continuation of the hydration reaction, and accelerates the strength gain. These processes are confirmed by high strength values at 7 days. Composite materials with percent moisture content at molding of 12 and 16 % correspond to the strength and frost resistance of grades M60 and M75, respectively. The composite material with a moisture content of 18 % during molding is not standardized, even for the highest grade M75, since the uniaxial compressive strength of the material exceeds the limit of 10 MPa and is 11.53 MPa

Thus, the composite material based on phosphogypsum of SE "Sirka" (Novyi Rozdil) when molded at the optimum moisture content for hydration processes meets the requirements of DSTU 9177-3:2022 "Crushed stone and gravel materials for road construction. Technical conditions. Part 3. Materials reinforced with mineral binders" and can be used as structural layers for road pavement.

5. Conclusions

Without intensifying the use of phosphogypsum in road construction, it will be impossible to achieve a high level of its utilization in Ukraine. The use of phosphogypsum materials in road construction is characterized not only by environmental and economic effects, but also allows to significantly improve the physical and mechanical properties of individual layers of the pavement structure and the pavement structure as a whole, while increasing the service life of roads. The possibility of effective use of long-term storage phosphogypsum (SE "Sirka", Novyi Rozdil) for the manufacture of composite materials for structural layers of pavement was established. The results of chemical and radiation analysis show that the phosphogypsum used meets the requirements of current Ukrainian standards. It is shown that the composite material based on phosphogypsum, blast furnace granulated slag, and Portland cement after 28 days corresponds in terms of compressive strength and frost resistance to grades from M10 to M75 (depending on the moisture content during molding). They are classified as water-resistant based on the value of the softening coefficient in water.

Abbreviations

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

References

Abdullah, H. H., Shahin, M. A., Walske, M. L., & Karrech, A. (2021). Cyclic behaviour of clay stabilised with fly-ash based geopolymer incorporating ground granulated slag. *Transportation Geotechnics*, *26*, 100430. doi: https://doi.org/10.1016/j.trgeo.2020.100430

Acikök, F. (2018). Effect of fly ash and ground granulated blast furnace slag on the strength of concrete pavement. *Journal of Sustainable Construction Materials and Technologies*, *3*(3), 278–285. doi: https://doi.org/10.29187/jscmt.2018.31

Arm, M. (2003). *Mechanical properties of residues as unbound road materials-experimental tests on MSWI bottom ash, crushed concrete and blast furnace slag*. Diss. Swedish Geotechnical Institute, Stockholm. Retrieved from https://www.diva-portal.org/smash/record.jsf?pid=diva2:1299982

Building materials. Phosphogyps Conditional for the production of gypsum binder and artificial gypsum stones, DSTU B V. 2.7-2-93 (1993).

Cánovas, C. R., Macías, F., Pérez-López, R., Basallote, M. D., & Millán-Becerro, R. (2018). Valorization of wastes from the fertilizer industry: Current status and future trends. *Journal of Cleaner Production*, *174*, 678–690. doi: https://doi.org/10.1016/j.jclepro.2017.10.293

Cao, J., Wang, Z., Ma, X., Yang, X., Zhang, X., Pan, H., & Luo, H. (2022). Promoting coordinative development of phosphogypsum resources reuse through a novel integrated approach: A case study from China. *Journal of Cleaner Production*, *374*, 134078. doi: https://doi.org/10.1016/j.jclepro.2022.134078

Chaimaâ, D. A., Khaled, L., Amina, A., & Kamal, E. O. (2022). Moroccan Phosphogypsum Use in Road Engineering: Materials and Structure Optimization. *Journal of Materials Science and Engineering A*, *12*(10-12), 115–130. doi: https://doi.org/10.17265/2161-6213/2022.10-12.002

Chernysh, Yu., Yakhnenko, O., Chubur, V., & Rubik, H. (2021). Pererobka fosfohipsu: ohliad ekolohichnykh problem, suchasni tendentsii ta perspektyvy. *Prykladni nauky*, *11*(4), 1575. doi: https://doi.org/10.3390/app11041575

Crushed stone materials and gravel materials for the road building industry. Part 3. The Materials bound by the mineral binders,DSTU 9177-3:2022 (2022).

Dvorkin, L. (2019*). Budivelni vyazhuchi materialy*. Rivne: NUVHP. Retrieved from https://ep3.nuwm.edu.ua/19090/1/%D0%91%D0%A3%D0%94_%D0%92%D0%AF%D0%96%D0%A3%D0%A7I_%D0%9C%D0%90%D0%A2%D0%95%D0%A0I%D0%90%D0%9B%D0%98.PDF

Dvorkin, L. Y., Dvorkin, O. L., Pushkarova, K. K., Kochevykh, M. O., Mokhort, M. A., & Bezsmertnyi, M. P. (2009). *Vykorystannia tekhnohennykh produktiv u budivnytstvi: Navchalnyi posibnyk*. Rivne: NUVHP.

International Fertilizer Industry Association. (2016). *Phosphogypsum: Sustainable Management and Use*. International Fertilizer Industry Association: Paris, France.

Ivashchenko, T. H., Bondar, O. I., Novoselska, L. P., & Vynnychenko, V. I. (2016). *Fosfohyps (ekolohichno bezpechni shliakhy utylizatsii ta vykorystannia): Monohrafiia*. Kherson: Oldi-plus

Kondratenko, N., & Shylovtseva, N. (2023). Realizatsiia pryntsypiv tsyrkuliarnoi ekonomiky u diialnosti mizhnarodnykh kompanii. *Ekonomika ta suspilstvo, 49*. doi: https://doi.org/10.32782/2524-0072/2023-49-28

Malanchuk, Z., Korniyenko, V., Malanchuk, Y., & Khrystyuk, A. (2016). Results of experimental studies of amber extraction by hydromechanical method in Ukraine. *Eastern-European Journal of Enterprise Technologies*, *3*(10(81)), 24–28. doi: https://doi.org/10.15587/1729-4061.2016.72404

Marushchak, U., Sanytsky, M., Pozniak, O., & Mazurak, O. (2019). Peculiarities of nanomodified portland systems structure formation. *Chemistry & Chemical Technology, 4*(13), 510–517.https://doi.org/10.23939/chcht13.04.510

Mozghovyi, V. V., Puhach, M. O., Mozghova, L. A., Kutsman, O. M., Chyzhenko, N. P., & Sokoliuk, M. Yu. (2014). Napriamky zastosuvannia zoloshlakiv TES u budivnytstvi avtomobilnykh dorih. *Visnyk Natsionalnoho transportnoho universytetu*, *29*(1), 199–205. doi: http://nbuv.gov.ua/UJRN/Vntu_2014_29(1)__26.

Natsionalna ekonomichna stratehiia na period do 2030 roku: Postanova KM 2021, No. 202 (2021).

Road Materials, Produced by cold recycling technology. Test methods, DSTU 8977:2020 (2020).

Smith, W., & Vorobieff, G. (2007, May). Recognition of sustainability by using stabilisation in road rehabilitation. *In Proceedings of the Australasian (Iron and Steel) Slag Association Sustainability and Slag Conference*. Retrieved from https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.608.5300&rep=rep1&type=pdf

Tayibi, H., Choura, M., López, F. A., Alguacil, F. J., & López-Delgado, A. (2009). Environmental impact and management of phosphogypsum. *Journal of environmental management*, *90*(8), 2377–2386.. doi: https://doi.org/10.1016/j.jenvman.2009.03.007

Tsioka, M., & Voudrias, E. A. (2020). Comparison of alternative management methods for phosphogypsum waste using life cycle analysis. *Journal of Cleaner Production*, *266*, 121386. doi: https://doi.org/10.1016/j.jclepro.2020.121386

Yakhnenko, O. M., Chernysh, Ye. Yu., Pliatsuk, L. D., & Trunova, I. O. (2015). Samozarostannia vidvalu fosfohipsu yak pokaznyk rivnia tekhnohennoho navantazhennia na dovkillia. *Ecological Safety and Balanced Use of Resources*, *1*(13), 110–119. Retrieved from https://ebzr.nung.edu.ua/index.php/ebzr/article/view/214

Yefimenko, A. S. (2021). *Pidvyshchennia vodostiikosti hipsu polifraktsiinymy mineralnymy dobavkamy*. Retrieved from http://lib.kart.edu.ua/handle/123456789/8225