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MODIFIED SULFUR CONCRETESWITH PHOSPHORIC SLAG FILLER

Abstract. The physico-mechanical properties of sulfur-asphalt concrete significantly exceed the standard parameters of conventional asphalt concrete. The use of sulfur-bitumen binders enhances the coefficients of heat resistance and crack resistance.

Microstructural studies have revealed the presence of thread-like crystals of polymer-modified sulfur in the composition of sulfur-bitumen binders, contributing to the micro-reinforcement of the binder.

Keywords: sulfur, phosphorus slag, bitumen, sulfur-asphalt concrete, compressive strength, production, quality control, modification, hydraulic construction.

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Introduction. The address of the President of the Republic of Kazakhstan, K. Zh. Tokayev, to the nation highlights the importance of water conservation and the reconstruction of highways [1]. In line with this directive, 4,000 km of highways are scheduled for reconstruction in Kazakhstan.

For efficient water usage, concrete-lined channels are proposed to replace earth channels [2].

To achieve this strategic goal, an estimated 1.1 million tons of bitumen, 1.5 million tons of mineral powder, and 10 million tons of coarse and fine aggregates will be required for road surfacing.

Resource base of Kazakhstan includes industrial by-products such as sulfur, slags, and thermal power plant ash [3].

The accumulation of sulfur as a by-product of petroleum refining and gas processing is growing rapidly due to the development of the oil and petrochemical industries.

Currently, more than 1 million tons of sulfur and over 10 million tons of blast furnace and phosphorus slags are stockpiled in Kazakhstan [2].

One promising direction in the modification of bitumen and the production of sulfur-asphalt concretes (SAC) is the use of sulfur, a high-tonnage by-product of petroleum refining.

Advantages of sulfur as an asphalt modifier include [3]:

– utilization of sulfur: Reducing storage and disposal costs.

– lower bitumen content: Replacement with sulfur without compromising quality.

– reduced investment: Savings on organic binders for road construction and maintenance.

– improved performance: Enhanced strength and operational characteristics of sulfur-asphalt concretes.

Recent studies [6] demonstrate that SACs are characterized by high strength and thermal stability. Researchers claim that these composites do not exhibit increased stiffness at low temperatures, making them less prone to plastic deformations in summer and cracking during winter.

In SACs, sulfur acts as a binder between bitumen and aggregate, providing high adhesive properties with charged microparticles on the aggregate's surface. This improves adhesion between bitumen and aggregate, resulting in enhanced physico-mechanical properties compared to conventional asphalt concrete.

Numerous studies address the compositions of SACs with fillers derived from blast furnace slag and thermal power plant ash. However, there is a lack of research on the use of glassy phosphorus slag as a filler for SACs.

Blast furnace and phosphorus slags are high-quality raw materials that undergo thermal treatment and are distinguished by stable chemical and mineralogical compositions [7].

Thus, the use of industrial waste, such as sulfur and slags, in the road and hydraulic construction industries is particularly relevant.

Objective of the Study: To develop compositions and investigate the physico-mechanical properties of modified sulfur-asphalt concretes with granular phosphorus slag fillers.

Materials and methods. For SAC production, the following materials were used: sulfur, bitumen, crushed stone, and phosphorus slag screenings. The phase composition of phosphorus slag was determined using a DRONE-3 X-ray diffractometer with a-SiC radiation and a nickel filter. X-ray parameters: U = 32 kV, J = 10 mA, and a counter rotation speed of 0,1 mm/sec. The microstructure of the sulfur-bitumen binder was studied with a JSM-7500F analytical scanning electron microscope equipped with an INCA Energy microanalysis system. Physico-mechanical properties of SACs were determined according to current regulatory documents.

Phosphorus slag is a by-product of phosphorus production formed during the electrothermal processing of phosphorite ores and additives. It is a gray, spherical material with a uniform structure and an average density of 2.7 g/cm^3. It has low porosity, minimal water absorption, and is resistant to acids and frost. It forms a satisfactory bond with bitumen. The main chemical components of phosphorous slag are calcium oxide (51%) and silicon dioxide (40%). The presence of up to 2% phosphorus pentoxide (P_2O_5) ensures the slag’s structural stability. As for the physical and mechanical properties, the true density is 2.92 g/cm^3, the average density is 2.85 g/cm^3, porosity is 1.1-1.5%, frost resistance is high (F100), losses during abrasion tests in the drum are up to 26%.

The high calcium oxide content (45-48%), porosity, and rough surface contribute to excellent adhesion with bitumen. On average, the adhesion of slag is 7-10% lower than limestone and 30% higher than granite [7,8].

Granulated phosphorous slag, which is produced by water-cooling molten slag at 1450°C, is considered as a porous material with an average density of 1200 kg/m^3.

Phosphorous slag consists of three phases: glass phase (90–95%), mineral phase (5-10%) and harmful gases (0.3-4%). The crystalline phase contains needle-shaped wollastonite crystals with characteristic interplanar distances (d/n): 4.21; 3.30; 3.05; 2.97; 2.29; 2.18 (Fig. 1).

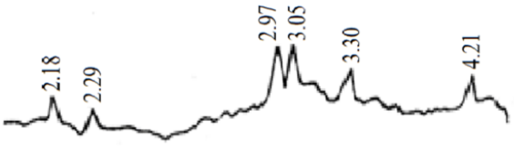


Fig. 1. Radiograph of phosphoric slag

A critical scientific and technical challenge in composite material design is establishing the relationship between composition, structure, properties, and manufacturing technology. The creation of sulfur composites should involve optimizing structure and properties at three hierarchical levels: sulfur binder, mastic, and concrete [4]. Phosphorous slag was tested as a mineral component for adhesion with sulfur-bitumen melt. The chemical activity of the phosphorous slag filler was evaluated using the following parameter [5]:

$$K_{hf}=K\tau\cdot Kp=\acute{\alpha}/\tau_0 Pt/Pe \qquad (1)$$

where: $K\tau$ – indicator of the influence of mixture porosity on mobility; τ_0 – shear stress limits of sulfur melt and mastic, respectively; α – empirical coefficient representing $\tau0\tau0$ as a function of vfvf; Kp – indicator of the filler's influence on mastic porosity; Pt; Pe – theoretical and experimental porosity of the material.

A critical K_{hf} value of 1 determines filler behavior, while with $K_{hf} \geq 1$, it is chemically inert filler, and within $0<khf<1$, it is chemically active filler.

For phosphorous slag, $K_{hf}=0.58$, indicating chemical activity. This significantly impacts the structural formation and properties of sulfur-bitumen binders.

Research results and discussion. Bitumen is an expensive and scarce component of asphalt concrete. Utilizing sulfur can partially replace bitumen while significantly enhancing road surface quality [1-3].

Granulated technical sulfur meeting GOST 127.1-93 standards was used for bitumen modification. This sulfur is a by-product of oil and gas refining at the Tengiz field. Main properties is given in table 1.

Table 1

The main properties of technical sulfur

Properties	Requirements of GOST127.1-93	Actual Value
Appearance	Yellow granules	Yellow granules
True density (kg/m³)	Not standardized	2065
Bulk density (kg/m³)	Not standardized	1060
Mass fraction of sulfur (%)	≥ 99.7	99.7
Mass fraction of ash (%)	≤ 0.02	0.01
Mass fraction of organics (%)	≤ 0.01	0.005
Mass fraction of acids (%)	0.0015	0.0012
Mass fraction of water (%)	0.2	0.1
Mechanical contamination (paper, wood, sand, etc.)	Not allowed	absent

The X-ray diffraction (XRD) pattern of sulfur (Fig. 2) exhibits peaks characteristic of orthorhombic and monoclinic modifications. The interplanar spacings are recorded at d=1.72; 1.76; 1.78; 1.90; 2.12; 2.43; 2.85; 3.11; 3.22; 3.34; 3.44; 3.87; 3.95; 4.06; 5.75; 7.76×10^{-10} m.

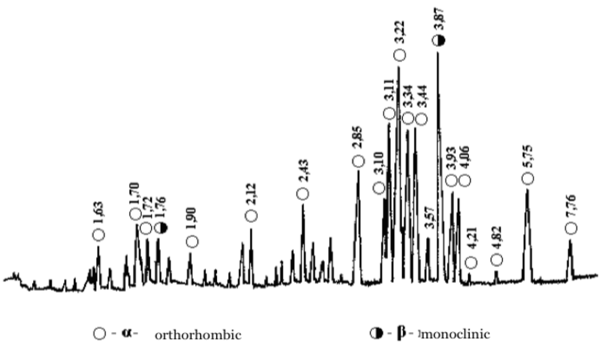


Fig. 2. X-ray of sulfur

Materials Used in the Development of Modified Sulfur-Asphalt Concrete (SAC):

– coarse aggregate: crushed stone (5-15 mm fraction) as per GOST 8267-93, with a bulk density of 1.59 g/cm³, sourced from Aysha Bibi.

fine aggregates:

– sand from crushing screenings as per GOST 8735-88 (Class II coarse sand), with a true density of 2,82 g/cm³ and bulk density of 1,67 g/cm³;

– mineral powder derived from phosphorous slag, with a true density of 2.72 g/cm³ and bulk density of 1,73 g/cm³, conforming to GOST R 52129-2003;

– binder: Bitumen grade BND 90/130, as per GOST 22245-90 (Aktau);

– sulfur as a by-product of oil production;

– modifier-polystyrene;

The composition of the mixtures is detailed in Table 2 below.

Table 2

Composition of sulfur-asphalt concrete mixture

№	Component	Mass Fraction
1	Crushed stone (3-10 mm)	60
2	Crushing screenings	32
3	Mineral powder	8.0
4	Bitumen 90/130, above 100%	4.1
5	Sulfur	1.2
6	Petrochemical resin	0.08

The study examined the physico-mechanical properties of asphalt concretes using the developed sulfur-bitumen binders.

Table 3 presents a comparative analysis of SAC produced using polysulfides and conventional asphalt concrete with BND 90/130 bitumen.

SAC with polysulfides as binders and phosphorous slag as filler demonstrates superior strength characteristics compared to asphalt concrete made with BND 90/130 bitumen.

The research highlights the feasibility of using polysulfides for developing sulfur-bitumen composites with phosphorous slag as a filler.

Table 3

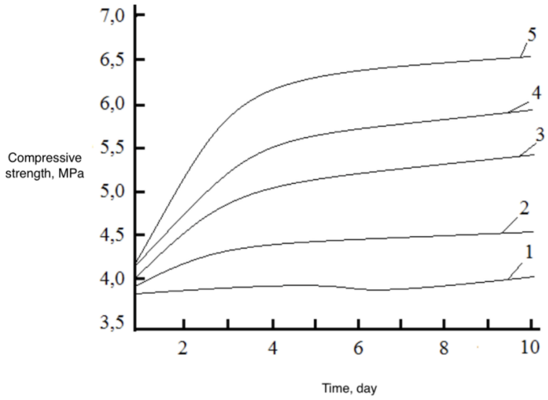
Comparative characteristics of sulfur asphalt concretes based on polysulfides and asphalt concretes based on bitumen BND 90/130

Parameter	SAC composition	GOST 9128–97 (Type B Asphalt Concrete)
Bulk density (g/cm³)	2.54	-
Water saturation (%)	0.52	2-5
Swelling (%)	0.1	-
Compressive strength limits (MPa)		
R_o	6.8	<12
R_{20}	4.33	>2.2
RB_{20}	3.74	-
R_{50}	1.62	>1
Water resistance KB (%)	0.97	>0.85
Water resistance under prolonged saturation	0.92	>0.85
Water saturation after 30 freeze-thaw cycles (%)	0.53	-
R_{20} after 30 freeze-thaw cycles	4.14	-
Frost resistance coefficient K_m (%)	0.98	-
Heat resistance coefficient R_{50}/R_{20}	0.43	-
Crack resistance coefficient R_{50}/R_{rack}	1.03	-

The development of this dispersed phase's characteristics occurs over time [4-6]. Accordingly, the kinetics of structure formation in sulfur-bitumen materials is of significant scientific and practical interest. Figure 3 illustrates the strength gain kinetics of asphalt concrete and sulfur-asphalt concretes with varying sulfur contents.

Analysis of experimental data (Fig. 1) reveals that, unlike asphalt concrete, sulfur-asphalt concrete demonstrates substantial changes in strength.

The figure indicates that the maximum strength increase is observed in sulfur-asphalt concrete with a sulfur content of 30%, while the control composition exhibits the lowest values. Notably, as the sulfur content increases, the strength of sulfur-asphalt concrete improves significantly over time.



1 – Control; 2 – Sulfur content (20%); 3 – Sulfur content (30%); 4 – Sulfur content (40%); 5 – Sulfur content (50%).

Fig. 3. The change in the strength of sulfur concrete from the hardening period

Microstructural studies of the modified sulfur-bitumen binder conducted using an analytical scanning electron microscope (JSM-7500F) equipped with the INCA Energy X-ray microanalysis system revealed (Fig. 4) the formation of a homogeneous mass with thread-like crystals of polymer-modified sulfur. These contribute to micro-reinforcement of the binder, thereby enhancing its physico-mechanical properties. Solid-phase reactions occur at the interface between the sulfur-bitumen binder and the mineral powder in the form of phosphorous slag, resulting in the formation of various compounds.

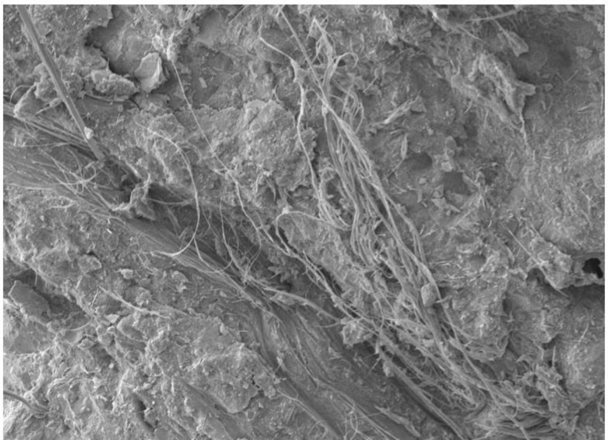


Fig. 4. Microstructure of sulfur-bitumen binder (magnification ×600,000)

In operational conditions, road surfaces are subjected to temperature fluctuations. As such, SAC must exhibit stable properties under varying temperatures.

To evaluate the stability of SAC properties under different climatic conditions, specific parameters are used: summer temperature variations – heat resistance coefficient $k_t = R_{50}/R_{20}$, and winter temperature variations – crack resistance coefficient $K_f = R_{50}/R_{crack}$. The results of these evaluations for the developed SAC compositions are presented in table 3. Analysis of the data indicates that the use of sulfur-bitumen binders in SAC led to an increase in the heat resistance and crack resistance coefficients. Specifically, heat resistance coefficient values exceeded the standard benchmarks by 25-30%, and crack resistance coefficient values surpassed the standards by 35-40%.

Since no universal method currently exists for assessing the climatic impact on asphalt concrete, the dynamics of physico-mechanical properties (compressive strength at 20°C and 50°C and tensile strength at 0°C) were studied under climatic influences according to established methodologies [7].

Climatic effects, especially cyclic temperature changes, cause the structure of SAC to degrade over time. This is due to binder aging and defect accumulation, which ultimately lead to a reduction in physico-mechanical properties.

The degradation coefficient $K_{\Delta R}$ was used to evaluate the impact of climatic factors on SAC properties:

$$K_{\Delta R} = 2/\Delta R_{20} + \Delta R_{50} + 1/\Delta R_p \rightarrow \max$$

where: ΔR_{20} – change in compressive strength at 20°C; ΔR_{50} – change in compressive strength at 50°C; ΔR_p – change in tensile strength at 0°C.

Crack resistance was evaluated based on tensile strength at 0°C with a deformation speed of 50 mm/min, according to GOST 12801-98. Results indicated that tensile strength values at 0°C ranged between 3.2-3.5 MPa. Higher $K_{\Delta R}$ values correspond to greater SAC stability.

After one simulated year of exposure to climatic factors, all sample compositions exhibited an increase in tensile strength and a decrease in compressive strength at 20°C and 50°C. This is attributed to binder aging, which reduces the concentration of light fractions in bitumen. Consequently, the material's brittleness temperature increased to 0°C, and stiffness rose at both 20°C and 50°C. The integral structural degradation value ($K_{\Delta R}$) was found to be 0.554, which is 20% higher than that of conventional asphalt concrete.

The cost of 1 ton of bitumen grade 70/100 is 220000 tenge, the cost of 1 ton of sulfur is 12000 tenge.When replacing bitumen by up to 40%, the economic effect per 1 ton of asphalt concrete at a consumption of bitumen of 38 kg and sulfur of 30 kg is about 6000tg.

Conclusion. Modified sulfur enhances the softening and brittleness temperatures while reducing the ductility and penetration of the sulfur-bitumen binder. Maximum compressive strength for SAC at 20°C reached 6.5 MPa. Calculated degradation coefficients demonstrate the influence of climatic factors on SAC's physico-mechanical properties.

Extended service life of sulfur-asphalt concrete is ensured by the optimal combination of crushed stone, screenings, bitumen, and sulfur, which provides strong adhesion between bitumen and aggregates. This reduces thermal-oxidative aging during production and application. Low residual porosity and minimal water saturation enhance water impermeability and provide superior water and frost resistance for the upper layers of road surfaces and hydraulic structures.

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ФОСФОР ҚОЖЫМЕН ТОЛТЫРЫЛҒАН МОДИФИКАЦИЯЛАНҒАН КҮКІРТТІ АСФАЛЬТБЕТОНДАР

Аңдатпа. Күкіртті асфальтбетонның физика-механикалық қасиеттері қарапайым асфальтбетонның нормативтік көрсеткіштерінен едәуір асып түседі. Күкіртті битумды тұтқыр затты қолдану жылуға төзімділік пен жарыққа төзімділік коэффициенттерінің мәндерінің артуына әкеледі.

Микроқұрылымдық зерттеулер құрамында күкірттің полимерлі модификациясының серобитумды тұтқыр жіп тәрізді кристалдарының болуын көрсетті,бұл тұтқыр заттың микроармациясына ықпал етеді.

Тірек сөздер: күкірт, фосфор қожы, битум, күкірт асфальтбетон, қысу беріктігі, өндіріс, бақылау, сапа, модификация, гидротехникалық құрылыс.

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МОДИФИЦИРОВАННЫЕ СЕРОАСФАЛЬТОБЕТОНЫ С НАПОЛНИТЕЛЕМ ИЗ ФОСФОРНОГО ШЛАКА

Аннотация. Физико-механические свойства сероасфальтобетона значительно превышают нормативные показатели обычного асфалтьобетона. Применение сернобитумного вяжущего, приводит к увеличению значений коэффициентов теплостойкости и трещиностойкости.

Микроструктурные исследования показали наличие в составе серно-битумных вяжущих нитевидных кристаллов полимерной модификации серы,которые способствуют микроармированию вяжущего.

Ключевые слова: сера, фосфорный шлак, битум, сероасфальтобетон, прочность при сжатии, производство, контроль, качество, модификация, гидротехническое строительство.