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СОДЕРЖАНИЕ

CLASSIFICATION OF MINERAL FILLERS USED IN ASPHALT CONCRETE

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Annotation: Mineral fillers are critical components of asphalt concrete, used to regulate structural formation processes and achieve composites with desired properties. This study aims to evaluate the surface-active properties of local mineral fillers using the RCA determination method developed by A.P. Nichiporenko. The findings demonstrate that different types of mineral fillers exhibit distinct surface energy characteristics, influencing the chemisorption activity of organic binders. By applying the Reduced Chemisorption Activity (P_{00}) as a classification criterion, we present a novel way to predict the behavior of fillers in asphalt compositions, providing a scientific basis for the selection of optimal fillers to enhance asphalt concrete performance. The study concludes that zeolite-containing rocks and other highly active fillers significantly improve the durability and mechanical properties of asphalt concrete.

Key Words: mineral fillers, Asphalt concrete, Surface-active properties, Chemisorption activity, RCA determination, Asphalt performance.

КЛАССИФИКАЦИЯ МИНЕРАЛЬНЫХ НАПОЛНИТЕЛЕЙ, ИСПОЛЬЗУЕМЫХ В АСФАЛЬТОБЕТОНЕ

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Аннотация: Минеральные наполнители являются важнейшими компонентами асфальтобетона, используемыми для регулирования процессов структурообразования и получения композитов с заданными свойствами. Целью данного исследования является оценка поверхностно-активных свойств местных минеральных наполнителей с использованием метода определения RCA, разработанного А.П. Ничипоренко. Результаты показывают, что различные типы минеральных наполнителей проявляют различные характеристики поверхностной энергии, влияющие на хемосорбционную активность органических вяжущих. Используя приведенную хемосорбционную активность (P_{00}) в качестве критерия классификации, мы представляем новый способ прогнозирования поведения наполнителей в асфальтобетонных композициях, обеспечивая научную основу для выбора оптимальных наполнителей для улучшения эксплуатационных характеристик асфальтобетона. В исследовании делается вывод, что цеолитсодержащие породы и другие высокоактивные наполнители значительно улучшают долговечность и механические свойства асфальтобетона.

Ключевые слова: минеральные наполнители, Асфальтобетон, Поверхностно-активные свойства, Хемосорбционная активность, Определение RCA, Эксплуатационные характеристики асфальта.

Introduction. Mineral fillers are a vital component in asphalt concrete, playing a crucial role in the regulation of the structural formation of asphalt mixtures and contributing significantly to their mechanical properties. These fillers enable the formation of building composites with targeted characteristics, thereby improving the overall performance of asphalt concrete in terms of durability and strength [1-4]. Despite their importance, there is a noticeable gap in the detailed study of the surface-active properties of mineral fillers, particularly regarding how these properties influence the interactions between mineral particles and organic binders.

To address this scientific gap, experimental studies were conducted at the Tashkent State Transport University to investigate the surface-active properties of local mineral fillers. The RCA (Reduced Chemisorption Activity) determination method, developed by A.P. Nichiporenko, was employed to comprehensively assess the acid-base and energy characteristics of the filler surfaces. This method offers significant advantages over previously used approaches, including the ability to classify the surface properties based on Lewis (aprotic) or Brønsted type, as well as determining the overall surface energy level. These aspects are critical for understanding the interaction mechanisms between mineral fillers and the asphalt binder.

The RCA method provides a multi-faceted evaluation, allowing for the determination of both the acidity or basicity of the filler surface and its energetic properties, which are directly linked to the strength of chemical bonds as represented by dissociation constants. By understanding these properties, we can predict how different fillers will interact with organic binders and ultimately impact the key operational properties of asphalt concrete—such as viscosity, strength, and frost resistance.

Materials and Methods. The mineral fillers investigated in this study included sand quartz, dune sand, gliej, basalt, electric smelting waste (EEP), copper smelting waste (WMP), fly ash from thermal power plants (TES), and zeolite-containing rock.

Experimental Procedure. The RCA determination method developed by A.P. Nichiporenko was utilized to assess the acid-base properties and surface energy levels of each filler. This method allows for the evaluation of whether the surface belongs to the Lewis (aprotic) or Brønsted type, as well as determining the surface energy level, which is linked to the strength of acid or base interactions. The adsorption centers (AC) were plotted and evaluated for their chemisorption activity based on the Lewis and Brønsted properties, which are essential for understanding the binder's performance.

In this study, the parameters derived from the RCA method were used to propose a new criterion for scientifically predicting the behavior of mineral fillers within asphalt concrete. This criterion, known as the indicator of Reduced Chemisorption Activity (P_{oo}), enables a systematic classification of fillers based on their impact on asphalt concrete properties. The results of this investigation, including the adsorption center distribution curves and detailed RCA measurements, provide insights that are crucial for optimizing filler selection to enhance asphalt performance.

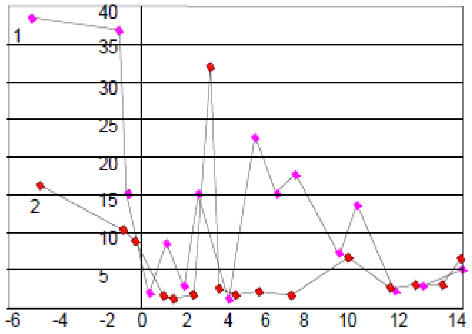

Fig. 1. Distribution of adsorption centers on the surface: 1 - basalt filler; 2 - TPP fly ash

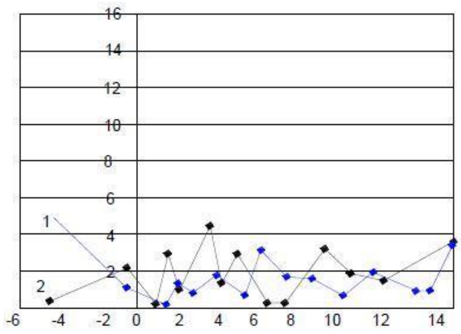

Fig.2 Distribution of adsorption centers on the surface: 1 - gluing; 2 - waste slag from electric smelting production

Table 1 and Fig. 1-5 show the results of determining RCA on the surface of mineral fillers accepted for study.

The distribution curves of adsorption centers (AC) of the surface of mineral fillers are plotted in coordinates:

$$g^{x}_{rKa} = F(rKA^{X}),$$

Where g^{x}_{rKa}- content of active sites, equivalent to the amount of adsorption indicator of a given acidic medium rKA^{X}, shown in Fig. 1-4.

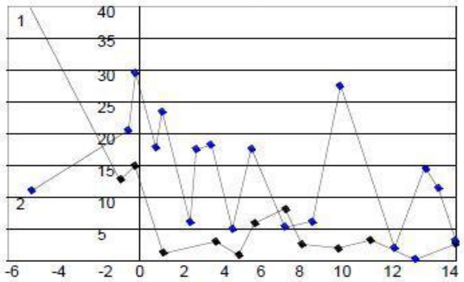

Fig. 3. Distribution of adsorption centers on the surface: 1 - zeolite-containing rock; 2 - quartz sand

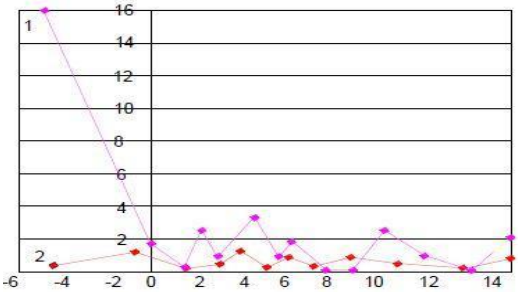

Fig. 4. Distribution of adsorption centers on the surface: 1 - waste slag from copper smelting production; 2 - sand dunes

To analyze the results obtained, it is more convenient to use the data in Table 1, which provides the values of the total activity of centers in a certain distribution area.

Such data are very valuable, as they allow us to evaluate the influence of each of them on the chemisorption process of the organic binder.

Table 1.

Content of surface adsorption centers of mineral fillers

№ n/p	Name of mineral filler	Number of centers, 10^3 mg-eq/m^2				General Qty centers
		-4…0	0…7	7…12,8	>12,8	
		R_{be}	P_{kb}	R_{ob}	R_{at}	
1.	Sand Quartz	8,04	9,11	8,75	1,88	27,78
2.	Dune sand	4,12	7,08	9,95	1,07	22,22
3.	Gliej	13,22	16,47	10,08	2,87	42,64
4.	Basalt	23,41	22,15	11,16	1,96	58,68
5.	EEP (electric smelting waste)	41,18	5,48	9,34	1,14	57,14
6.	WMP (copper smelting waste)	6,61	23,88	16,37	4,32	51,18
7.	Zola- unos TES	43,14	27,61	11,77	5,32	87,84
8.	Zeolite containing rock	102,08	24,88	12,62	2,14	141,72

Table 1 summarizes the content of adsorption centers for each mineral filler. The fillers' surface-active properties varied significantly, with the zeolite-containing rock exhibiting the highest number of centers, indicating its potential as a highly reactive filler. The results demonstrated the varying impact of each filler on the energy levels and interaction potential with organic binders.

The findings indicate that mineral fillers play a crucial role in determining the overall performance of asphalt concrete. The high chemisorption activity observed in zeolite-containing rock and basalt suggests that these fillers could substantially enhance the binder's adhesion to aggregate, leading to improvements in strength, durability, and frost resistance. These results align with previous studies [6, 7], confirming that surface properties of fillers influence their interaction with organic binders.

The classification criterion (P_{oo}), introduced in this study, is based on the reduced chemisorption activity of mineral fillers, and helps categorize fillers into weakly active, moderately active, highly active, and superactive types. Zeolite-containing rock and fly ash, categorized as superactive fillers, have demonstrated more than a 15% increase in the strength of asphalt concrete.

The practical implications of this study are significant, particularly in the construction industry. By selecting highly active mineral fillers, it is possible to enhance asphalt properties, resulting in longer-lasting road surfaces with reduced maintenance costs.

In the works of Yadykina N.N. [7] confirmed the hypothesis formulated by her that, based on the structure of the surface of mineral rocks and the composition of bitumen, it can be concluded that the molecules of organic substances, contained in the binder can interact quite actively with surface of acidic mineral materials. For example, aromatic polycyclic structures included in asphaltenes and resins, including heterocycles with nitrogen and sulfur, having π bonds and atoms with lone electron pairs, can be electron donors and interact with electron-withdrawing acid Lewis sites (pKa > 13). Moreover, condensed aromatic compounds contained in asphaltenes, resins and oils are more unsaturated than benzene, so they are much more active. In addition, side substituents in the form of limiting aliphatic chains, as well as other substituents with a +C effect (-OH, -OR, -OCOR, -SH, -NH2, -NHR) activate benzene rings. Naphthenic rings, containing, for example, nitrogen, are also strong Lewis bases, and pyridine, according to [8], easily forms complexes with aprotic acids, which are Lewis acid sites on the surface of silica.

Complex compounds of phenols and nitrogenous bases are also capable of forming donor-acceptor bonds with acid sites Lewis (pKa > 13) surface.

At Brønsted acid sites, which are surface hydrosilic groups (pKa 0-7), hydrogen bonds can be formed with the participation of a surface hydrogen atom, exhibiting electron-acceptor properties, as donors in the formation of these bonds can be π - bonds, that is, electrons of benzene nuclei and multiples bonds of organic compounds of bitumen, as well as unshared electronic pairs of heteroatoms. Numerous studies have been conducted [9], it is clear show that the adsorption of polar molecules or aromatic compounds

through π bonds occurs most strongly on surface silanol groups that are not hydrogen bonded to neighboring OH groups. Therefore, to achieve maximum adsorption, the silica surface should not contain adsorbed water, but should have the highest concentration of SiOH groups.

According to Hair and Ellis [9], the strongest adsorption of organic compounds occurs on isolated hydroxyl groups with unperturbed vibrations located on a thermally dehydrated silica surface. Aromatic hydrocarbon molecules interact with similar hydroxyl groups in a 1:1 ratio. Bitumen also contains nitrogenous bases and compounds containing hydroxyl (-OH), carbonyl (-C=0), ester (-COOR) and other groups that form during the oxidation of oil residues, which are Brønsted bases and will interact with Brønsted acid centers surfaces.

Other functional groups with an oxygen atom (-COOH, $R\text{-}C^{+}\text{=}0$), as well as free oxygen compounds - naphthenic and asphaltogenic acids, anhydrides, phenols are also capable of adsorbing on the active surface centers of silica-containing mineral materials.

Acids will naturally interact with basic Brønsted centers (pKa 7-13), moreover, aromatic acids are stronger than aliphatic ones, and the presence of two substituents, for example, -COOH and -OH, in naphthenic and aromatic rings, which is often observed in the composition of bitumen, increases the acidity, and, consequently, the adsorption capacity of these compounds.

In [10], when considering the mechanism of reactions on the surface of silica, it is indicated that during the adsorption of organic acids, it is likely chemisorbed compounds are formed.

Acid anhydrides (R-C^O-O-CO-R) are electron acceptors, therefore, they are able to interact with electron-donating Lewis bases (pKa < 0). From organic substances, organic compounds containing n-bonds conjugated with substituents with a greater -C effect, which are Lewis acids, can also be adsorbed at these centers. In bitumens these can be compounds with groups SO_3N^+ и NO_2^+, but their number is very small.

We cannot exclude the possibility of the formation of hydrogen bonds or even the transfer of a proton as a result of the acid-base interaction of bitumen acids and basic Lewis centers of the silica surface, but in non-polar environments this is unlikely.

Thus, from the above we can conclude that, contrary to traditional opinion, the surface of acidic silica-containing mineral materials is not inert with respect to the components of bitumen. The interaction at the interface between organic binder and mineral material cannot be considered in a simplified manner, from the point of view that the surface of acidic rocks is negatively charged, and bitumen contains surfactants of predominantly anionic type (asphaltogenic and naphthenic acids), so interaction between them is practically impossible. It is necessary to take into account the presence on

On the surface of mineral materials, not only the thinnest colloidal films of oxides and hydroxides and amorphous silica, but also the presence of active surface centers that can adsorb almost all organic compounds contained in bitumen and thereby provide strong adhesive contacts between the binder and the surface of mineral materials.

Taking these circumstances into account, as well as taking into account the insignificant influence of the intensities of adsorption centers on the surface of mineral fillers in the pKa region from -4 to 0 on the chemisorption activity of the organic binder, we proposed a criterion that allows us to evaluate the surface-active properties of mineral fillers in asphalt concrete. This criterion was called the indicator of reduced chemisorption activity and is designated by the symbol P_{please}. This indicator is calculated based on the results obtained after studying the donor-acceptor properties of the surfaces of mineral fillers using the indicator method for determining the distribution of adsorption centers (RCA) according to the method of Nechiporenko A.P. [5]. As is known, a complete description of the acid-base properties of the surface of mineral fillers involves determining the concentration and strength of active centers, i.e. obtaining their distribution differentiated into acidic and basic according to Lewis and Brenstad.

Having the results of determining the distribution of adsorption centers on the surface of mineral fillers, it is quite easy to calculate the indicator of the reduced chemisorption activity of a given filler, which is determined by the formula:

$$P_{please} = P_{at}+0,5P_{kb}+0.25P_{at}, \tag{1}$$

where, R_{at}, P_{ol}, P_{at} – number of adsorption centers in the areas: pKa >13.0;

0<rKa<7; 7<rKa<13.0 in 10^{-3} mEq/g. respectively.

This criterion characterizing the acid-base properties of the surface of mineral fillers makes it possible to scientifically classify mineral fillers according to the degree of their impact on the quality indicators of asphalt concrete. In general, the following classification of mineral fillers is proposed according to criterion - P_{please}, that is, according to the indicator of reduced chemisorption activity calculated using formula (1) (Table 2).

For mineral fillers accepted for research, the calculation of this criterion, i.e., the indicator of reduced chemisorption activity, was carried out in tabular form and is presented in Table. 2.

Table 2.

Classification of mineral fillers according to the reduced chemisorption activity P_{please}

№ n/p	Types of mineral fillers	Criterion values P_{please}	Potential efficiency in asphalt concrete composition, % increase in strength
1.	Weakly active	from 0< to. <10	Up to 5%
2.	Moderately active	from 10< to. <15	5-10%
3.	Highly active	from 15< to <20	10-15%
4.	Superactive	Over to >20	more than 15%

Analysis of the results of calculating the P criterion$_{please}$ (Table 3.) shows that, according to the proposed classification, the local mineral fillers accepted for the study belong to the following types according to chemisorption activity: ground dune, quartz sand, OEP - moderately active; basalt, zeolite-containing rock - highly active; WMD, fly ash from thermal power plants are super active.

Table 3.

The scoring criterion P_{please} in tabular form

№ n/p	Name of mineral filler	Initial data				Converted Data		Criterion P_{please}
		-4…0	0…7	7…13,0	>13,0			
		R_{be}	P_{kb}	R_{ob}	R_{at}	$0.25p_{ob}$	$0,5\ P_{kb}$	
1.	Sand Quartz	8,04	9,11	8,75	1,88	2,18	4,55	8,61
2.	Dune sand	4,12	7,08	9,95	1,07	2,49	3,54	7,10
3.	Gliej	13,22	16,47	10,08	2,87	2,52	8,23	13,62
4.	Basalt	23,41	22,15	11,16	1,96	2,80	11,07	15,83
5.	OEP waste from electric smelting production	41,18	5,48	9,34	1,14	2,33	2,74	6,21
6.	OMP-Copper smelting waste	6,61	23,88	16,37	4,32	4,09	11,94	20,35
7.	Zola intake	43,14	27,61	11,77	5,32	2,94	13,80	22,06
8.	Zeolite containing rock	102,08	24,88	12,62	2,14	3,15	12,44	17,73

In order to confirm the reliability and correctness of the obtained research results on the development of a new criterion for assessing the surface-active properties of mineral fillers for asphalt concrete, we conducted comparative studies with the previously obtained research results of other scientists and specialists [11-17]. Calculation results of the proposed criterion P_{please} for mineral fillers studied in the works of N.N. Shangina, V.V. Yadykina. [6,7] show that the proposed criterion for assessing the surface-active properties of mineral fillers based on the reduced chemisorption activity (P_{please}) quite correct and objectively reflects the potential chemisorption capacity of a given type of filler in asphalt concrete.

Thus, the proposed criterion for assessing the acid-base properties of the surface of mineral fillers according to the P index$_{please}$ shows high convergence with the results of previously cited studies and can be taken as the basis for predicting and regulating the physical, mechanical and operational properties of asphalt concrete.

Conclusion. This study classified mineral fillers used in asphalt concrete based on their surface-active properties and chemisorption activity. The novel RCA determination method allowed for a comprehensive analysis, revealing that highly active fillers like zeolite-containing rock and fly ash from thermal power plants can significantly improve the mechanical properties of asphalt concrete. The proposed classification criterion, P_{oo}, provides a scientific basis for selecting optimal mineral fillers, thereby enhancing asphalt performance and longevity.

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