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# The Influence of Active Adsorption Centres of the Surface Dispersed Material on the Interaction with Bitumen

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**Abstract:** The interaction of bitumen with mineral materials from acid rock with the active adsorption centres on the surface has been theoretically justified. The paper also studies the donor-acceptor properties of mineral powders, their adsorption capacity with respect to the bitumen. In also discusses the properties of bituminous mixtures based on mineral powders of various rocks. It is concluded that in the preparation of organic composites one must consider not only the chemical composition of mineral components, but also the state of the surface, namely, the presence of active adsorption centres.

**Key words:** Bitumen % Mineral materials % Surface adsorption centres % Bituminous composites

## INTRODUCTION

To address the problem of improving the quality and durability of a material one of the limiting factors is the strength of the bonds between the binder and the aggregates at the interface. The main role in these processes is played by the surface of the dispersed material that is different from the volume increased energy potential [1-5].

It is known that each active surface area of the mineral materials used for the production of organic composites, absorbs a certain kind of polar groups. But in general, the entire surface can be characterized as a certain amount of active zones of the charge. The surface of most of the major species is charged positively and the most acidic is charged negatively.

The study of surface properties of the particulate oxides, in particular silica, is a significant part of the present work. It is known that adhesion, chemical and catalytic properties of solids depends on the chemistry of the surface geometry and [5-6]. Moreover, the surface properties of particulate fillers do not always correspond to its composition and properties within the scope and vice versa. It is important to note that not the entire surface but only its active centres are involved in the adsorption of [6-7], so that they will primarily determine the reactivity of the mineral material and to participate in the interaction with the binder. The active silica surface is determined by the degree of hydroxylation of the surface.

Taking into account the shortage of conditioned rubble and sand and the large number of man-made materials, in particular, along with the rocks produced in mining operations and the products of their concentration, the urgency of its use has increased.

Most man-made materials are acidic and, as commonly believed, they do not provide adequate adhesion to bitumen.

However, information on the donor-acceptor properties of the surface of mineral materials used for the production of asphalt, their impact on the interaction with the bitumen and the properties of the bituminous composites in the literature is limited.

## MATERIALS AND METHODS

The aim of this work was to study the donor-acceptor properties of the surface of the dispersed material from both traditional raw materials and from man-made, to establish their influence on the interaction with an organic binder and on the main physical and chemical characteristics of bituminous composites.

Objects of the study were of acidic mineral powders with a surface area of rocks 400 $m^2$/kg, prepared quartz sandstone, granite and silica sand and limestone. Chemical composition of the investigated mineral materials is shown in Table 1.

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Table 1: The chemical composition of the mineral material

| The content of oxides by weight. % | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Quartz sandstone | | | | | | | | | | | |
| $SiO_2$ | $Al_2O_3$ | $TiO_2$ | $Fe_2O_3$ | FeO | CaO | MgO | $P_2O_5$ | $Na_2O$ | $K_2O$ | MnO | LOI |
| 92.76 | 1.90 | 0.10 | 0.04 | 2.08 | 0.51 | 1.09 | - | 0.19 | 0.21 | - | 0.85 |
| Quartz sand | | | | | | | | | | | |
| 93.2 | 2.2 | | 0.8 | - | 2.2 | 0.2 | - | 0.2 | - | - | 0.7 |
| Granite | | | | | | | | | | | |
| 69.9 | 14.8 | 0.4 | 1.6 | 1.7 | 2.1 | 1.0 | 0.3 | 3.3 | 4.1 | 0.1 | 0.7 |

To study the donor-acceptor properties of dispersed materials we used the indicator method of fixing the distribution of adsorption centers (DAS). This method based on the change in the solution colour under indicator adsorption on active solid surface centers allows to estimate the number of active centres on the particular type of the acid value [8] and characterize the surface activity with respect to the binder.

The nature of the interaction with the surface of the bitumen mineral materials was judged by its adsorption of the benzene solution and desorption of adsorbed organic binder, as well as changes in the IR spectra of the bitumen after contact with various mineral powders. Clutch organic binder with mineral materials was determined by the adsorption of methylene blue and the gravimetric method. Physical and mechanical properties of sandy asphalt concrete were determined by standard methods.

**The Main Part:** To purposefully structure asphalt concrete one should consider in more detail the nature of the interaction of acidic mineral materials with bitumen, thus highlighting the features and capabilities of each of the interacting components in view of the properties of the surface.

According to the modern concepts [6-7], the solid surface is bi-functional as it a scope centers of Lewis and Brensted of both acidic and alkaline types. In this case, the materials traditionally related to acidic can have a sufficient number of major centers and vice versa.

Based on the study of active surface centres in terms of the adsorption of various acid value indicators pKa, a donor-acceptor model of the solid body, presented in the form of the distribution spectrum of adsorption centres (DAS) has been created [8]. Four fields-Lewis's alkaline centers (pKa ranging from 4 to 0), Brensted's acid centers (pKa ranging from 0 to 7) and alkaline centers (pKa ranging from 7 to 13) and Lewis's acid centers (pKa is more than 13) were allocated on the scale.

The existing is generally accepted definitions of acid and base according to Brensted and Lewis are also apllied to organic compounds that make up the bitumen.

Lewis's acid centers are organic compounds containing [pi]-bonds, integrated with substitutes having a greater [ce]-effect its amount in bitumen is little. Lewis's centers are compounds containing atoms with lone electron pairs and [pi]-bonds (including aromatic and heterocyclic compounds).

Based on the analysis of the solid surface and the composition of bitumen, we have concluded that the molecules of organic substances contained in the binder can be enough to interact with the surface of acidic mineral materials and schemes of possible interactions [9].

Thus, it can be concluded from the above that in spite of traditional point of view, the surface of acidic siliceous mineral materials are not inert and its interaction with the bitumen's to be considered in view of the active surface centres which can adsorb substantially all organic compounds contained in the bitumen and provide a strong adhesive contact between the surface of the binder and mineral materials.

The implementation of the proposed schemes is possible in case of availability of the sufficient number of active centres on the surface of the particulate materials used as mineral components of asphalt mixtures. The largest contribution to this interaction will make a Lewis's acid centers, acid and alkaline Brensted's centers.

Determination results of the total amount of adsorption centres on the surface of dispersed powders, presented in Table 2 indicate a significant difference in activity of the surface investigated mineral materials. Moreover, both the number of various types of adsorption centers and the total content of the active centers differ.

Based on the traditional ideas, anionic substances mainly determine bitumen activity against mineral materials, so they interact with the Brensted's alkaline centers [10], whose amount is larger on the quartz

Table 2: The content of adsorption centers, $\times 10^3$ mc-eq/g

| Mineral material | Brensteda acid centers | Brensteda alkaline centers | L'yuisa acid centers | Total active centers |
|---|---|---|---|---|
| Quartz sandstone | 14.28 | 10.56 | 1.97 | 26.81 |
| Granite | 12.28 | 6.60 | 1.10 | 19.98 |
| Quartz sand | 10.0 | 7.80 | 0.45 | 18.25 |

Table 3: The adhesion of mineral materials with bitumen

| | Bitumen adhesion on the mineral material determined by the method the "dye", % | | | |
|---|---|---|---|---|
| Mineral material | Quantity of bitumen before boiling | Quantity of bitumen after boiling | Coefficient of adhesion stability | Adhesion bitumen by the gravimetric method,% |
| quartz sandstone | 77 | 65 | 0.84 | 76 |
| granite | 76 | 46 | 0.60 | 65 |
| quartz sand | 62 | 30 | 0.48 | 48 |
| limestone | 84 | 74 | 0.88 | 78 |

sandstone surface than on the granite and quartz sand surface. Furthermore, the total number of active centres on the surface quartz sandstone is also higher than the conventional mineral materials, so in view of the theoretical assumptions outlined above, it follows that the greatest activity with respect to the bitumen will exhibit quartz sandstone mineral powder.

The active component adsorbed on the surface of the bitumen quartz sandstone is confirmed by IR spectroscopic studies in terms of reduction in the amount of aromatic, naphthenic compounds, acidic groups of the bitumen after its interaction with a mineral powder of quartz sandstone; in case of the contact with quartz sand such no changes were observed.

Since the molecules of organic compounds that make up the bitumen, are complex and contain a wide variety of functional groups, there is reason to believe that there will be a strong adsorption and irreversible [5, 11].

The results of the adsorption-desorption of benzene bitumen solutions indicate that the surface quartz sandstone irreversibly adsorbs more than 60% bitumen, whereas the surface of the quartz sand of the same composition-only 25 %. This indicates a significant contribution of chemical bonds in the process of adsorption on the surface of the bitumen mineral material.

The study of adhesion of mineral materials with bitumen showed a clear correlation with the concentration of this magnitude of the Lewis's acid centers and the acid and alkaline Brensted's centers, as well as the amount of active surface centres with the acid value more than 7 and more than 0. The correlation coefficients ranged from 0.90 to 0.97.

To assess the adhesion of the mineral material and bitumen the indicators of the coupling method of dye adsorption and gravimetric method were determined.

The research results (Table 3) show that the ability of quartz sandstone and sand, having nearly identical chemical and mineral composition, to hold bitumen film on their surfaces are completely different and , quartz sandstone in terms of this indicator is closer to limestone, which is the main rock as compared with to granite and quartz sand.

A similar pattern of adhesion to the surface of bitumen mineral materials can also be seen in the study of photographs bituminous materials from which it is clear that almost the entire surface is covered with a film of bitumen quartz sandstone, unlike quartz sand (Fig. 1).

Thus, it has been found that in case of the interaction of bitumen with quartz sandstone the formation of chemical bonds occurs due to the presence of active adsorption centres on the surface that makes a good grip with the bitumen, which should positively effect the properties of bituminous mixtures.

The bituminous mixtures properties of matter "bitumen-mineral powder" have a significant impact on the quality of the asphalt, so the study of the properties of bituminous mixtures (Table 4) provides for the most complete picture of the interaction of the studied mineral material and asphalt, as well as the prediction of the properties of asphalt concrete on such materials, as it is the nature of the interface and primarily the adhesive interaction of extremely concentrated dispersion that determines the properties of composite materials and their stability during use.

The study of bituminous mixtures shows that the content of silicon dioxide ($SiO_2$) in the mineral material is of a large, but not essential importance for interaction with the bitumen. When using quartz sandstone bituminous mixtures has the highest indicators and the use of quartz sand-the lowest, even though they have very similar chemical and mineral composition.

Table 4: Physical and mechanical properties of bituminous mixtures

| Physical and mechanical properties of asphalt concrete samples | Mineral powder | | | |
|---|---|---|---|---|
| | quartz sandstone | granite | quartz sand | limestone |
| Water content, % | 2.32 | 2.55 | 2.94 | 1.95 |
| Average density, kg/m$^3$ | 2320 | 2310 | 2210 | 2100 |
| Swelling, % | 2.50 | 2.63 | 2.73 | 2.01 |
| Compressive strength, MPa at | | | | |
| 50 °C | 2.8 | 2.6 | 2.1 | 3.0 |
| 20 °C | 6.4 | 6.1 | 5.1 | 7.0 |
| in water-saturated state at 20 °C | 5.2 | 4.5 | 3.8 | 6.0 |
| Water resistance | 0.81 | 0.74 | 0.68 | 0.86 |

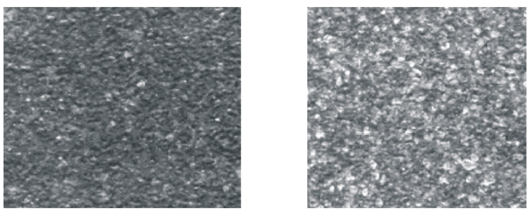


Fig. 1: Adhesion of bitumen on the surface of mineral materials

Thus, the compressive strength in case of compressionat 20° and 500° samples of bituminous mixtures for quartz sandstone is 6.4 and 2.8 MPa, whereas quartz sand-5.1 and 2.1 MPa, and the coefficient of water resistance-0.81 and 0.68 respectively.

## CONCLUSION

The surface of acid silica-containing mineral materials is not inert and its interaction with the bitumen must be viewed in the context of active surface centres that can absorb practically all the organic compounds available in the bitumen and thus providing a strong adhesive contact between the surface of the binder and mineral materials. This interaction has a positive effect on the properties of bituminous mixtures.

**Findings:** A decisive influence on the interaction with the bitumen has the nature of its surface, but not chemical and mineral composition of the filler, that is, the number of active adsorption centres on it. A clear-cut correlation between the contact of adsorption centres on the surface of fillers and their activity in the interaction with bitumen has been established, providing the correct cohesion, which structures the effect of the physical and mechanical characteristics of bituminous mixtures.

The above refutes study the established points of view regarding the inefficient use of mineral materials from acidic rocks in organic composites.

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