Method of Modifying of Mineral Fillers for Asphalt Concrete by Calcium Polysulfide

Sergey Inozemtcev¹, Evgeniy Korolev¹

¹ Moscow State University of Civil Engineering, Yaroslavskoe shosse, 26, Moscow, 129337, Russia

inozemcevss@mgsu.ru

Abstract. The method of modifying the surface of grains of mineral filler for asphalt concrete with calcium polysulphides is presented in the paper. Calcium polysulfide solution has been proposed for the expansion of the mineral resource base in the production of asphalt concrete aggregates, which breaks down into elemental sulphur and calcium hydroxide in the course of filler modification. The proposed modifier reduces the temperature coefficient for the bitumen-mineral binder by 1.8 times. The structure of the composite of highly filled mixtures based on modified filler has higher properties compared to mixtures based on classical filler: compressive strength at temperature 0°C – up to 33.5%; Compressive strength at a temperature of 20°C – up to 84%; Compressive strength at a temperature of 50°C – up to 34.3%.

1. Introduction

The filler is the most important component of the asphalt mixture, which is responsible for the formation of the structure of asphalt concrete. The structure of bitumen changes at the interface with the interaction of mineral filler with bitumen. Features of the interaction of bitumen with mineral filler affect the quality of adhesion to the surface and the thickness of the resulting layer, which differs from the properties of volume bitumen in its physical, mechanical and rheological properties. The use of mineral fillers of different mineralogical composition is associated with the specifics of their interaction with the active components of bitumen. Several methods for determining the thickness of the bitumen layer with modified structure parameters are developed: a method based on theoretical approaches Deryagina B.V. [1], rheological method [2], calculation method [3] and others. However, some of them require thorough substantiation.

Carbonate mineral powder is traditional filler in asphalt mixes. Using of mineral powders from non-carbonate rocks, solid and powder industrial wastes is allowed. These materials should not contain oxides $\text{Al}_2\text{O}_3+\text{Fe}_2\text{O}_3$, $\text{P}_2\text{O}_5$ and active compounds $\text{CaO}+\text{MgO}$ more than 1.7%; 2.0% and 1.7%, respectively.

The using of activated mineral powders derived from carbonate rocks with the addition of anionic or cationic surfactants (surfactants) or products containing surfactants with bitumen as activating substances is allowed. Higher carboxylic acids, amines, diamines, and their derivatives are used to improve the surface activity of the grains of the mineral powder.
However, in regions where the use of carbonate filler is not economically feasible, it is more rational to produce filler from local raw materials. To improve the activity of mineral materials from local raw materials, various types of surface modifying agents are used. Thus, in order to expand the mineral resource base used for the production of asphalt concrete fillers, the actual direction is the development of a technology for the functional modification of mineral powder.

Traditional surface modifiers for mineral filler are fatty tar, polyphenols, synthetic fatty acids, oxidized petrolatum, etc. [4-6].

Usually, the surface activation of the grains of mineral powder is carried out using surfactants or their mixture with bitumen, which increase the adhesive properties of the binder.

The authors developed [7] a modifier for mineral powder based on a mixture of heavy tar and the residue of the production of household synthetic detergents - alkyl sulphate, which increases the hydrophobicity of the filler, reduces swelling and consumption of bitumen during the preparation of the asphalt-concrete mixture.

In [8], a method for obtaining a mineral powder that is activated by a complex additive based on liquid fatty acids and reinforcing fibres from cellulose, asbestos, and basalt is proposed.

The use of filler activated by a mixture of fatty tar and soluble wood resin allows increasing the high-temperature properties, the water resistance of asphalt concrete and to reduce the content of bitumen in the mixture [9]. In [10], wood-chemical materials in a mixture of wood resin of conifers and tall oil were used to activate the mineral powder, which forms chemical adsorption layers chemically bound by the –OH and –COOH active groups during the physicochemical reaction. Asphalt concrete based on the filler, activated wood chemical reagents, has high strength at 50 °C and strength at 0 °C.

In [11, 12], the results of a study of a nanomodified filler of porous silicon powder and surface modifier based on sols of iron hydroxide and silica acid are presented. The use of a nanomodifier in the composition of the asphalt concrete mixture allowed to increase the resistance to rutting and weather and climatic factors.

Modification of the surface of the mineral filler can be carried out by various compounds, including compositions containing nanoparticles. There are very few studies of the effect of primary nanomaterials on the physicochemical properties of mineral filler. It should be noted that the identification of the influence of the size effect of the modifier particles on the physicochemical characteristics of the mineral filler is an additional task.

2. Materials and methods

Traditional dolomite mineral powder was used to study the effect of modifying the mineral filler by calcium polysulfide.

In this work, calcium polysulfide CaSₙ solution (“Lime-sulphur decoction”) was used as a modifier for mineral filler. Calcium polysulfide CaSₙ is produced in LCC “IC KHMTEK” by technical regulations of the organization TU 2153-003-55841212-2003 “Aqueous solution of calcium polysulfide. Technical conditions”.

BND 60/90 bitumen (Moscow Refinery LLC) was used to study the properties of bitumen-mineral binder based on a mineral filler modified by calcium polysulfide (table 1).

| Table 1. Main properties of the bitumen BND 60/90 |
|-----------------------------------------------|
| Properties                            | Requirements | Actual value |
| Penetration at 25°C, 0.1 mm             | 61–90        | 66           |
| Penetration at 0 °C, 0.1 mm             | more 20      | 37           |
| Ductility at 20 °C, cm                  | more 55      | 80           |
| Ductility at 0°C, cm                    | more 3.5     | 3.6          |
| Softening point, °C                     | more 47      | 53           |
Brittleness, °C  

| Changing of softening point after aging, °C |
|------------------------------------------|
| no more -15                              |
| no more 5                                |

Processing of the mineral filler modifier was carried out in accordance with the following procedure:

1. Mixing the mineral powder with a solution of calcium polysulfide in a planetary mixer in ratios by weight:
   - solution of CaSₙ / MP = 0.125;
   - solution of CaSₙ / MP = 0.25;
   - solution of CaSₙ / MP = 0.375.

2. Drying of the modified filler in a dry-heat oven at a temperature of 70 °C for 12 hours. Calcium polysulfide molecules break down into elemental sulphur and calcium hydroxide at the drying stage.

3. Grinding of modified mineral filler in a ball mill (if necessary).

Bitumen-mineral binders with a volume degree of filling of 0.1, 0.2, 0.3 and 0.4 were made to study the rheological properties. The compositions of the bitumen-mineral binder are presented in table 2.

Table 2. The composition of the bitumen binder

| Filler | 0   | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  | 11  | 12  | 13  | 14  | 15  | 16  |
|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Bitumen| 1.0 | 0.9 | 0.8 | 0.7 | 0.6 | 0.9 | 0.8 | 0.7 | 0.6 | 0.9 | 0.8 | 0.7 | 0.6 | 0.9 | 0.8 | 0.7 |
| MP     |     | 0.1 | 0.2 | 0.3 | 0.4 |     |     |     |     |     |     |     |     |     |     |     |
| CaS-1  |     |     | 0.1 | 0.2 | 0.3 | 0.4 |     |     |     |     |     |     |     |     |     |
| CaS-2  |     |     |     | 0.1 | 0.2 | 0.3 | 0.4 |     |     |     |     |     |     |     |
| CaS-3  |     |     |     |     | 0.1 | 0.2 | 0.3 | 0.4 |     |     |     |     |     |     |

Notes: MP – mineral powder; CaS-1 – MP, modified calcium polysulfide in the ratio of CaSₙ/MP = 0.125; CaS-2 – the same CaSₙ/MP = 0.25; CaS-3 – the same CaSₙ/MP = 0.375;

Figure 1. The typical rheological curve of a dispersed system with non-Newtonian properties [10]

Figure 2. Example of thixotropic properties of the bitumen binder (vf = 0.4; CaSₙ/MP = 0.25)

Determination of the rheological properties of the bitumen-mineral binder was carried out on rheometer MCR 101 Anton Paar using the measuring system: coaxial cylinders. Measurements were carried out at temperatures in the range from 110 to 140°C under conditions of variable shear rate from 1 to 3500 s⁻¹: the highest viscosity limit of the practically not destroyed structure (η₀); the lowest
limiting viscosity of the extremely destroyed structure (\(\eta_m\)); boundary stress for a practically not destroyed structure (\(P_r\)); the boundary stress for the ultimate destruction of the structure (\(P_m\)) and the conditional yield strength for the dynamic ultimate shear stress (\(P_k\)).

The particle size distribution of dispersed phase particles in a calcium polysulfide solution was determined using the laser diffraction method on a Zetatrurc analyzer.

The changes in the elemental composition of the mineral filler were determined by energy dispersive spectroscopy using an integrated FEI Quanta 200 X-ray microscope.

The strength of samples from a mixture of bitumen with mineral powders was determined on the cylindrical samples (diameter 50.5 mm, height 50.5 mm) under uniaxial compression after exposure in the water at the desired temperature for at least 1 hour.

Porosity (voids in total mix – VTM) of the cylindrical samples was calculated by the formula:

\[
V_p = \left(1 - \frac{\rho_m}{\rho}\right) \cdot 100\%,
\]

where \(\rho_m\) – average density, g/cm\(^3\); \(\rho\) – true density, g/cm\(^3\).

### 3. Results and discussions

Due to the instability of the molecules, calcium polysulfide decomposes into elemental sulfur and calcium hydroxide during the preparation of the modified mineral filler. Complex surface relief of the mineral powder is formed, which represented by both nano- and micro-sized objects (figure 3).

![Figure 3. Grading of CaSn particles in solution](image)

The logical consequence is an increase in the area of the phase interface (table 3). The chemical composition of the surface of the mineral filler is enriched with calcium and sulfur (table 4).

| Indicator                  | MP  | CaS\(_n\)/MP |
|----------------------------|-----|--------------|
| Grading, %                 |     |              |
| less 2.0 mm                | 100 | 100          |
| less 0.125 mm              | 100 | 100          |
| less 0.063 mm              | 87  | 98           |
| Average density, g/cm\(^3\)| 1.77| 1.76         |
| True density, g/cm\(^3\)  | 2.63| 2.60         |
| Porosity, %               | 33  | 32           |
| Bitumen indicator, g     | 56  | 55           |
| Surface area (BET),m\(^3\)/g| 21.3| 71.3         |

Table 3. Main properties of the mineral fillers modified particles of sulfur
Table 4. Elemental content of the mineral fillers

| Elements | The content of the element in the mineral filler, % | MP  | CaS$_n$/MP |
|----------|--------------------------------------------------|-----|------------|
| O        |                                                  | 48.2| 46.3       |
| Mg       |                                                  | 15.3| 13.6       |
| Al       |                                                  | 2.1 | 1.9        |
| Si       |                                                  | 6.4 | 5.6        |
| Ca       |                                                  | 25.9| 29.6       |
| Fe       |                                                  | 2.1 | 2.5        |
| S        |                                                  | –   | 0.5        |
| **Total**|                                                  | 100.0| 100.0  |

The calculation of the structural parameters of the modified filler was made on the basis of the experimental data obtained. The structural parameters selected are as follows:

- the ratio of the thickness of the modifier layer $h_s$ to the particle diameter of the mineral filler $d_0$:

$$
\frac{h_s}{d_0} = \frac{1}{2} \left( \frac{1}{\frac{\rho_f}{S_f}} \right) \left( 1 - \frac{v_f}{v} - 1 \right),
$$

- (2)

- the ratio of the area of the structural elements of the modifier layer $\bar{s}_{1,m}$ to the surface area of the particle mineral filler $\bar{s}_{1,0}$:

$$
\frac{\bar{s}_{1,m}}{\bar{s}_{1,0}} = \left( \frac{S_{f,m}}{S_{f,0}} \right) \left( \frac{\rho_{mf}}{\rho_f} \right) \left( 1 + 2 \frac{h_s}{d_0} \right)^3,
$$

- (3)

- the ratio of the average size of the structural element of the modifier layer to the particle diameter of the mineral filler:

$$
\bar{l} = \left( 1 - \frac{S_{f,0}}{S_{f,m}} \right) \left( \frac{\rho_f}{\rho_{mf}} \right);
$$

- (4)

where $\rho_{mf}$, $\rho_f$ and $\rho_s$ – the densities of the modified filler, mineral filler and modifier, respectively; $S_{f,m}$ and $S_{f,0}$ – specific surfaces area of the modified filler and the original mineral filler, respectively; $K_s$ – shape factor of the structural element of the modifier layer (for the cubic form, $K_s = 6$).

The structural parameters of the modifier layer and the average size of the structural element of the modifier layer are presented in table 5. The average linear size of the structural element of the modifier layer increases significantly with increasing content of the modifier (calcium polysulfide). The increase in size is non-linear in nature (figure 4). The increase in size is non-linear in nature (figure 4). This indicates that more perfect crystalline decomposition products of calcium polysulfide can form with increasing content of the modifier.
Table 5. Structural parameters of the modifier layer and the average linear size of the structural element of the modifier layer

| CaSₙ/MP | Structural parameters | l, nm |
|--------|-----------------------|-------|
|        | h/d₀  | slₘ/sl₀ | l/d₀  | l*, nm |
| 0.125  | 0.009 | 3.50    | 0.0157| 472.4  |
| 0.25   | 0.016 | 4.21    | 0.0233| 698.2  |
| 0.375  | 0.042 | 5.26    | 0.0519| 1556.1 |

Note: * – when d₀ = 30 μm.

Figure 4. The dependence of the change in the size of the structural element of the layer modifier from the ratio CaSn/MP

Theoretical calculations show that the size effect manifests itself to particles with a size of no more than 10–20 nm [16, 17]. The calculations (table 5) indicate that it is impossible to establish the influence of the size effect of the structural elements of the modifier on the properties of the bitumen-mineral binder. A possible positive effect from the formation of smaller structural elements of the modifier is their substantially rapid dissolution. This follows from the Thomson equation [18]:

\[
\ln \left( \frac{C(r)}{C_\infty} \right) = \frac{2\sigma V_m}{\kappa RT},
\]

where \( C(r) \) and \( C_\infty \) – solubility of a particle with radius \( r \) and particles with a small radius of curvature; \( \sigma \) is the surface tension; \( V_m \) – molar volume; \( R \) – universal gas constant; \( T \) – temperature.

With other things being equal (temperature and time of preparation of the bitumen-mineral binder), the main effect of the modification should depend on the concentration of the modifier, and not on the dispersion of the products of the decomposition of calcium polysulphides.

The results show that an increase in the number of modifiers slightly changes the average density, reduces the true density, which is explained by an increase in the volume of lighter sulphur in the bulk of the material. Filling micro- and macropores of the filler with modifier conversion products lead to a decrease in the porosity of the mineral powder. There is a decrease in the bitumen capacity of the filler compared with MP for the same reason, and an increase in the content of the modifier leads to an increase in this indicator.
The change in the surface properties of the mineral material contributes to the change in the processes of interaction with bitumen and the properties of dispersed systems based on modified filler. The modifier influences the change in the structure of the boundary layers occurs in the process of interfacial interaction of bitumen and mineral filler. Changing the features of structural transformations in the system affects the technological and rheological properties of the mixture [14, 15].

Surface modification of the mineral filler will contribute to the change in the properties of the surface layers of bitumen and will affect the properties of dispersed systems based on it. The effect of the modification will presumably increase with an increase in the concentration of the modifier.

 dependences of changes in the rheological parameters of the bitumen-mineral binder of various compositions on temperature are presented in figure 5.

Figure 5. Changes in the rheological properties of bitumen-mineral binder of various compositions (Number 0 ... 16)

Analysis of the presented experimental data shows that the change in the rheological properties of bitumen-mineral binders occurs when the amount of the studied mineral powders and the degree of surface modification of the grains of the mineral filler is changed.

The influence of the degree of surface modification of mineral filler grains with calcium polysulphides is assessed by analysing the dependences of temperature coefficients of changes in the viscosity of bitumen-mineral binder melts (thermosensitivity) for the practically intact $K_0$ and extremely destroyed $K_m$ structure (figure 6). These coefficients are proposed to evaluate as follows [10]:
\[
K_0 = -\frac{d \lg \eta_0}{dT},
\]
\[
K_m = \frac{d \lg \eta_m}{dT},
\]

where \( d \lg \eta_0 \), \( d \lg \eta_m \) – changing of viscosity limit of the practically not destroyed structure and changing of the lowest limiting viscosity of the extremely destroyed structure; \( dT \) – changing of temperature.

\[\begin{align*}
K_0 &= -30.539x + 145.35 \\
K_0 &= -22.904x + 139.59 \\
K_0 &= -15.269x + 133.83 \\
K_0 &= -7.6346x + 128.06 \\
K_m &= -1.0147x + 127.53 \\
K_m &= -0.7610x + 121.79 \\
K_m &= -0.5074x + 116.06 \\
K_m &= -0.2537x + 110.32 
\end{align*}\]

**Figure 6.** Dependencies of the change in the temperature coefficients of the binder with a different degree of filling on the content of the calcium polysulfide for: a) practically not destroyed structure; b) extremely destroyed structure

Analysis of the results of calculating the temperature coefficient of the bituminous binder based on a modified filler shows that an increase in the content of the modifier does not lead to a decrease in viscosity and, as a consequence, to a decrease in the temperature coefficient. The temperature coefficient of the practically not destroyed structure decreases by 10–20%. The modifier on the surface of the grains of mineral filler reduces the viscosity of the melt bitumen-mineral binder at a lower temperature and increases the processability of bitumen-mineral mixtures based on the modified mineral filler.

The structural characteristic of the elements of the modifier layer \( \bar{l} \) is an important parameter. The effect of \( \text{CaS}_n/\text{MP} \) and \( \bar{l} \) is estimated from the slope (rate of change of the function) of the corresponding dependence. The calculation results (table 6) convincingly demonstrate the dominant influence of the amount of the \( \text{CaS}_n/\text{MP} \) modifier.

**Table 6.** The rate of change of viscosity from the content of calcium polysulphides and the size of the structural parameters \( \bar{l} \)

| Parameters                  | Value of parameters for different degree filling |
|-----------------------------|-----------------------------------------------|
|                             | 0.1   | 0.2   | 0.3   | 0.4   |
| Viscosity change rate on \( \bar{l} \), \( \cdot 10^3 \) | 0.04  | 0.05  | 0.06  | 0.07  |
| Viscosity change rate on \( \text{CaS}_n/\text{MP} \) | 0.14  | 0.21  | 0.25  | 0.28  |

Changes in the properties of highly concentrated dispersed systems on cylinder samples with the same bitumen content of 15.4% and porosity (voids in total mix – VTM) from 4 to 5% were studied. The change in the bulk properties of samples from the content of a modifier on the surface of filler is presented in figure 7.
Figure 7. Dependence of changes in water saturation and swelling of samples from a mixture of bitumen with a mineral powder on the content of the surface modifier

An analysis of figure 7 shows that an increase in the amount of modifier contributes to decreasing water saturation and swelling. It happens because the compaction of the mixture improves and the wetting of the material decreases, which complicates the penetration of water into the pores and defects. This effect contributes to an increase in the water resistance of the samples after saturation with water in a vacuum (figure 8a). 

The compressive strength at different temperatures reflects the quality of the interaction between the mineral material and bitumen, which shows the degree of the structuring of the binder and the force of adhesion of the grains to each other (figure 8b-d).

Figure 8. The dependence of changes in the properties of samples from a mixture of bitumen with a mineral powder on the content of the surface modifier: a) water resistance; b) compressive strength at 0 °C; c) the same at 20 °C; d) the same at 50 °C
Strength at different temperatures increases with increasing content of modifier, which confirms the increase in the degree of the structuring of bitumen on the surface of the grains and their adhesion to each other.

Modifying by calcium polysulfide allows to control the properties of the mineral filler and produce composites with high strength and water resistance. It is a prerequisite to produce the asphalt with high physical-mechanical and performance properties.

4. Conclusions
1. The average linear size of the structural element of the modifier layer increases significantly in non-linear dependence with an increase in the content of the modifier (calcium polysulfide). This indicates that with an increase in the content of the modifier, more perfect crystalline decomposition products of calcium polysulphides may form.
2. It is established that the viscosity and temperature coefficient of the bitumen-mineral binder decrease with an increase in the amount of modifier on the surface of the filler. The temperature coefficient of the practically unbroken structure of binder decreases by 10…20% and the temperature sensitivity of the maximally destroyed structure of binder does not change with an increase in the content of the modifier. This leads to an improvement in the processability of mixtures using fillers modified with calcium polysulphides.
3. The structure of the material from highly filled mixtures based on mineral powder of calcium polysulphide-modified possesses enhanced properties in comparison with mixtures on MP-1 according to the following indicators: compressive strength at 0 °C - up to 33.5%; compressive strength at a temperature of 20 °C - up to 84%; compressive strength at a temperature of 50 °C - up to 34.3%.
4. The developed method of modifying mineral materials with calcium polysulfide will expand the mineral resource base used for the production of asphalt concrete fillers.

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