Advanced Materials Research Vols. 1079-1080 (2015) pp 58-61
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doi:10.4028/www.scientific.net/AMR.1079-1080.58

Submitted: 25.09.2014
Revised: 17.10.2014
Accepted: 25.10.2014

Sulfur-extended High-performance Green Paving Materials

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Keywords: sulfur-bituminous concrete, green concrete, pavements.

Abstract. Currently, there is a strong need of high-performance and environment-friendly paving materials in Russian Federation. The demands for such materials, together with parameters of the existing production facilities, heightened interest in modification of bitumen with cheap and broadly available components. The results of numerous studies of sulfur-extended asphalt concretes are summarized in the present work. For the suppression of hydrogen sulfide and sulfur dioxide we propose to use the complex nanoscale modifier. The application of such modifier allows to increase the amount of sulfur in constructional mix, thus increasing the mobility of the mix during laying and escalating the values of operational properties – most notably compressive strength and resistance to rutting. The application of designed material leads to the decrease of environmental load in regions near the oil and gas industry enterprises.

Introduction

There are recent trends in developing of environment-friendly alternatives to common construction materials. By convention, the material has to be considered as a "green" if at least one of the following conditions is met: a) there is a relatively low pollution to the environment during production of the material and/or exploitation of the construction made of such material; b) constructional mix includes low-cost industrial by-products and/or wastes which otherwise have to be dumped and pollute environment; c) the material includes components (e.g. photocatalytic admixtures) which causes decomposition of the environmental-unfriendly mediums (nitrogen oxides etc.).

High values of the operational properties usually are not required for green building materials. But common consequence of using the materials with poor operational properties is low service life and high operational costs. Therefore, such materials are of low economic efficiency and not in demand in the market. Moreover, due to low service life of the construction there is an increase of environmental loads; this is because requirements for production of extra amount of building materials.

Thus, to be competitive with traditional construction materials, new green ones have to possess high operational properties, which lead both to economical efficiency and reduced load to the environment.

Nanomodifiers and nanomodified building materials

At present, there are numerous examples of successful application of nanotechnology in material science and civil engineering [1]. Probably, the most known application in road construction is the photocatalytic coverings and bulk materials with photocatalytic admixtures. For example, admixture of nanoscale titanium dioxide, which can be bound to different carriers [2, 3] notably decreases the content of nitrogen and sulfur oxides in the air near the roads, thus reducing the environmental pollution by exhausts of vehicles [4]. The efforts can also be directed not only to reduction of the air pollution, but also to improvement of entire complex of operational properties. The term "Nanomodification" covers the different nanotechnology processes targeted to creation of nanoscale structures inside the material; the presence of such structures may lead to numerous improvements: strengthening of constructional composite, prolongation of service life, simplification of production and usage.

The strengthening is the most common target. There are methods of application of both inorganic [5] and organic [6] additives which leads to increased compressive strength of the building materials. The mechanical properties of nanoscale-modified constructional composites, including ones with bituminous matrix, are subject of extensive examination – both experimental [5-8] and numerical [9-11].

Sulfur-extended building materials for pavements

There are cases when achievements of modern material science combined with proper mix design and production technology lead to design of economically effective green building materials with improved operational properties. One of such materials is sulfur-extended green asphalt concrete. The admixture of sulfur to bitumen during the production of asphalt concrete is a known way to improve the properties of the paving. The method of modifying bitumen with sulfur had been used for the first time about one hundred years ago. The large-scale activities in this area were initiated in the end of XX century.

The feasibility of the sulfur-bituminous asphalts is caused by properties, availability and low cost of sulfur. In Russia, there are many sulfur dumps near the oil industry enterprises. Such dumps consumes a lot of area which otherwise could be occupied by vegetation, contributing to the improvement of the environmental situation. Incorporation of sulfur in bulk building materials contributes to decrease of load to the environment.

At present, the advantage of using modified sulfur binder in road construction is practically assured. The preparation of materials with composite sulfur-bituminous binder can be carried out with existing equipment, thus lowering costs required to adjustment of the production cycle.

The known factor limiting the use of the sulfur-extended materials was the lack of methods to neutralize the hydrogen sulfide and sulfur dioxide formed during the manufacture and installation of sulfur-bituminous pavements. Thus, the traditional sulfur-bituminous concrete in no conditions can be considered as a green building material.

Nanoscale suppressor of toxic gases

To reduce the emission of toxic gases, the production and laying temperatures may be reduces. For non-degassed technical sulfur, the source of hydrogen sulfide is the gas enclosed in the pore space of granules; the gas is released upon melting. But the requirement of low temperature increases laying complexity and in general is not sufficient. At the time, there was no effective method to perform sorption of toxic gases from the sulfur-modified asphalt mixes. The primary reason for such a situation was insufficient knowledge about the processes of interaction between sulfur and bitumen [12]; examination of processes occurring during production of the sulfur-bituminous concrete is quite difficult due to complexity of the structural transformation.

To overcome the principal drawback of the traditional sulfur-bituminous concrete, we have designed several nanoscale admixtures for the sulfur-bituminous paving materials. The sulfur is subject to chemical reactions with unsaturated components of resins and alkenes. This leads to formation of various compounds. To ascertain the influence between composition, technology and emission of toxic gases during preparation of sulfur-extended asphalt, the chemical reactions were examined in detail and analysis of the energy balance for various paths of H_2S and SO_2 formation was carried out [12]. The results gave us insight of possible ways to suppress the emission of toxic gases. The designed neutralizer consists of two components. Component “A” is for preventing the dehydrogenation of bitumen, and nanoscale component “B” is for bonding the hydrogen sulfide and sulfur dioxide into insoluble complexes. The availability and local cost of components were taken into account during the selection of particular substances as components “A” and “B”. The most advanced solution to suppress the emission is to use complex sulfur-based modifier consisting of sulfur and neutralizer mixed together. The neutralizer reduces emissions of hydrogen sulfide and sulfur dioxide down to safe values; results of experimental investigations are summarized in Table 1.

Table 1.

Parameter	Interaction time, [min]					
	15	30	60	15	30	60
	values for SO_2			values for H_2S		
Maximal emission, mg/m^3	2.0	6.0	8.6	0.6	2.1	3.0
Reduction rate	9.8	4.3	2.6	11.0	7.1	6.1

As if follows from Table 1, the designed complex admixture greatly reduces the emission of toxic gases, especially emission of hydrogen sulfide. This simplifies the technology of laying during the construction of pavements.

Mechanical properties of sulfur-extended paving materials

To gain the technical and economical efficiency, new sulfur-extended asphalt concretes have to be characterized by improved operational properties. This is especially important for pavements on large-span road constructions under dynamic loads, eg. cable-stayed bridges [13]. But till now there was limited knowledge about physical and mechanical properties of the concrete with sulfur-bituminous matrix.

To determine strength and resistance to rutting, we had performed the laboratory tests according to RU GOST 12801, RU GOST 31015 and AASHTO TP 63.

It was confirmed that admixture of sulfur greatly increases the mechanical properties of asphalt. Starting from concentration of 20%, there is linear dependence between strength and amount of sulfur is observed; adding the sulfur significantly alters the properties of the asphalt binder (the concentrations above 40% can not be used in practice because several other operational properties of the concrete are out of allowed limits).

There is one operational property which is tightly correlated with mechanical properties – resistance to rutting. Low values of rutting resistance significantly reduce durability of the pavement under load of heavy vehicles.

It was found during laboratory tests (we were using APA testing machine for AASHTO TP 63 examination) that even the small amount of sulfur significantly increases rutting resistance. Therefore, the area of primary application of sulfur-bituminous concrete is the construction of pavements with heavy load.

Some mechanical properties of the designed materials are presented in Table 2.

Table 2.

Property	RU GOST 31015	Ref. sample	Modified concrete		
			20% of S	30% of S	40% of S
Compressive strength at 20 ^{0}C, MPa	not less than 2.2	3.34	3.35	4.15	5.30
Compressive strength at 50 ^{0}C, MPa	not less than 0.65	1.67	1.72	2.19	2.82
Clutch shear (50 ^{0}C), MPa	not less than 0.18	0.29	0.29	0.38	0.54
Long-term water resistance	not less than 0.85	0.90	0.89	0.95	0.90

As it can be decided from the Table 2, compressive strength of sulfur-bituminous concrete exceeds not only the corresponding values for reference samples, but also values required by RU GOST 31015.

Summary

The designed paving material offers an economically effective, long-life alternative to traditional concretes. The novelty of the material is in special nanoscale admixture designed to significantly decrease the emission of sulfur dioxide and hydrogen sulfide. The material combines strength necessary for prolonged operation with flexibility to perform extra-quality pavement. Prolonged service life of constructions, reduced air pollution and utilization of industrial by-products during production make the developed material environmental-friendly. Usage of the designed materials decreases the costs of exploitation of roads, especially in regions with huge temperature swings.

Acknowledgements

This work is supported by the Ministry of Science and Education of Russian Federation, job No 7.11.2014/K, project title “Theoretical and experimental study of the dynamics of constructions”.

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