Mater. Res. Soc. Symp. Proc. Vol. 1611 © 2014 Materials Research Society
DOI: 10.1557/opl.2014.762

New Alumosilicate Fillers Based on Sedimentary Rocks for Asphalt Concrete

Valeria Strokova[1], Mikhail Lebedev[1], Irina Potapova[1] and Konstantin Sobolev[2],
[1]The Belgorod State Technological University named after V.G. Shoukhov, Belgorod, Russia
[2]Department of Civil Engineering and Mechanics, University of Wisconsin-Milwaukee, Milwaukee, USA

ABSTRACT

Asphalt concrete is the most common material for highway and motorway construction. The quality of asphalt is determined, to a large extent, by properties of asphalt binder. Fillers, which are mineral powders from carbonate rocks and aggregates fines, such as limestone and dolomite, are often used in the composition of bitumen mastics affecting the performance of asphalt.

This article explores the feasibility of using the fines of aluminosilicate sedimentary rocks as fillers. These materials are composed of clay minerals, which change their properties upon the contact with water. Normally, the use of such fillers is restricted because of poor water resistance and swelling of asphalt concrete. In order to improve the performance of these fillers, the thermal modification at moderate temperatures of 500–600 ^{o}C has been proposed. Such treatment provides sufficient structural stability of obtained materials and results in the reduction of water absorption of asphalt, improved water resistance (up to 2.5 times) and also, in reduced swelling (up to 9 times).

It has been demonstrated that improvement in the filler performance can be achieved by a heat treatment. Such treatment induces changes in the mineral composition and converts the structure of clay minerals into the frame structure of zeolite, as confirmed by X-ray diffraction and infrared spectroscopy. Due to thermal treatment, there is a change in the acid-base properties of the surface of the filler, which is reflected in the profiles of the main adsorption centers. As a result, due to chemisorption, the modified aluminosilicate fillers are able to interact with bitumen. The application of new filler materials in asphalt concrete enables to enhance the performance.

INTRODUCTION

The construction of asphalt pavements in Russia requires the application of a range of mineral materials such as rocks and waste products [1, 2].

The expansion of raw materials supply is possible by the use of large deposits of sedimentary rocks [3, 4]. Weathering and sedimentation genesis make these materials the most complex polymineral systems, based on quartz and silica-aluminates. However, these materials may demonstrate unstable properties, which complicate their use in the production of building materials. Still, these materials can be used as mineral fillers for asphalt binders and asphalt concrete.

Changes in the crystal and chemical characteristics of clayly soils and improvement of physical and mechanical properties can be facilitated by modification, activation, [4–6] and thermal modification is proposed as the most appropriate approach [11–13].

According to available literature [4–8], the thermal treatment improves the pozzolanic properties characterized by lime absorption, and increases the adsorption activity and the adhesion to highmolecular compounds such as bitumen. Therefore, the resulting filler materials can be used as supplements for conventional inorganic fillers [9].

Earlier studies on the lime adsorption processes carried on the hydraulically active burned rocks of Kuzbass and also the model systems revealed that the greatest amount of adsorption occurred in clay materials treated at 500 °C, and reduced with an increase in firing temperature from 500 to 1000 °C [5–8]. In this work thermal treatment at the range of temperatures from 400 to 600 °C is used to improve the performance of fillers.

EXPERIMENTAL PROGRAM

The compatibility of fillers for bituminous minerals is studied by using the aluminosilicate rocks of Paleozoic, Lower Mesozoic, Upper Cretaceous and Cenozoic sediments of the Southern Ural supplied from the coal mine areas; these materials are considered as typical representatives of the sedimentary rocks in Russia. The range of raw materials for this study is supplied from the deposits of coal mine “Korkinskoe”.

The investigated samples are represented by predominantly claylу materials (Table 1), with inclusions of siliceous biogenic residues (gaize and gaizeleous clay) and carbonaceous matter.

Table 1. The Basic Properties of Investigated Silicoaluminate Materials

Destination of samples / Characteristics	Coal bearing sandstone, aleurolite, argillite	Coal-bearing rocks: sandstone, aleurolite, argillite	Gaizeleous clay	Gaize
Specific Gravity	1.90	2.58	2.32	2.38
Hydroscopic moisture, %	4.91	1.89	3.72	0.97
Plasticity index	-	9.4	25	7
Soil classification	Fine-grained sand	Light silty clay loam	Pulverescent clay	Light silty clay loam
Al_2O_3/SiO_2 ratio	High ratio		Low ratio	
	0.36	0.25	0.14	0.10
	Reduction of Al_2O_3/SiO_2 ratio			
Distinctive features	Inclusions of carbonaceous matter	Mostly clay material	Mostly clay material	High content of opal

The presence of these inclusions causes the loss of plastic properties, which are inherent to clay minerals. According to X-ray analysis, the tested samples have similar mineral composition with the presence of quartz, clay minerals (kaolinite, Ca-montmorillonite, hydro-micaceous minerals), mica (biotite) and feldspar (albite, anorthite). Some of these have a crystalline structure, but there is a significant quantity of pseudocrystalline and X-ray amorphous phases, which should also include amorphous carbon material and cristobalite-tridymite (CT) opals.

Based on their chemical and mineral compositions all the samples can be conditionally divided into two groups with low and high Al_2O_3/SiO_2 ratios (Table 1). Considering the composition and characteristics of the tested materials these can be further grouped into four types (Table 1):

- with a high Al_2O_3/SiO_2 ratio doped with carbonaceous matter;
- with a high Al_2O_3/SiO_2 ratio, predominantly clay composition;
- with a low Al_2O_3/SiO_2 ratio, predominantly clay composition;
- with a low Al_2O_3/SiO_2 ratio and high content of opal.

In this investigation, the materials are dried in an air oven and milled in a ball mill for a surface area of 430–870 m^2/kg.

The thermal treatment at 400, 500 and 600 C^o is conducted for 2 hours in an oven. The processed materials are milled in a ball mill for a surface area of 570–1050 m^2/kg to achieve the homogeneity of the filler.

The physical properties measured are specific gravity (SG), particle size distribution (PSD) by laser diffraction, surface area (SA) and Rigden voids (RV) by compacting under pressure of 40 MPa. The chemical and mineral compositions are determined using X-Ray diffraction and X-Ray Fluorescence (XRD/XRF). The test for bitumen capacity is equal to a quantity of industrial oil per 100 cm^3 of the filler to reach a certain consistency. The optimal content of bitumen in the mix with the powder corresponds to water saturation of specimens within 4–5 %. These specimens are produced by compacting a mix in the molds under the pressure of 10 MPa. Water saturation of asphalt binder is measured by storing in a vacuum apparatus filed with water for 1 hour under the negative pressure of 0,002 MPa. The specimens with optimal bitumen content are subjected to further testing for water resistance and swelling. The water resistance coefficient characterizes the reduction of compressive strength of the specimens after water exposure in a vacuum. Swelling is related to an increase of specimen's volume of bitumen binder after saturation with water in vacuum conditions, followed by heating.

EXPERIMENTAL RESULTS

The properties of the obtained fillers are listed in Table 2. Because of their mineral composition and structure the aluminosilicate materials are fine grained divided substances with a high grindability important for their use as mineral powders.

The performance characteristics are determined for asphalt binder mastics based on investigated alumosilicate sedimentary rock materials. According to Table 3, the strength of water-saturated samples is reduced by 39–55%. The presence of a hydrophilic clay results in the high swelling (from 9.3 to 19.4%). Features of the rocks of sedimentary strata, consisting of layered alumosilicates have a detrimental effect on the physical and mechanical properties of asphalt binders (Table 3 and Table 4).

According to the performed research, the thermal treatment of raw materials causes the changes in mineral composition, and, as a result, modifies the surface absorption sites. The temperatures of 500–600 ^oC are the most suitable for the synthesis of skeletal formations of aluminosilicate materials.

Table 2 – The Main Characteristics of Mineral Powders and Mastics

Sample type		Thermal treatment	Performance Characteristics					
			Specific surface, m^2/kg	Specific gravity	Porosity, %	Moisture, %	Bitumen capacity, g	Optimal bitumen content, %
Standard requirements			-	-	≤ 40	≤ 2.5	≤ 80	-
↓↓↓↓↓ Reduction of Al_2O_3/SiO_2 Ratio ↓↓↓↓↓↓↓↓	Sample with high Al_2O_3/SiO_2 ratio, coal-bearing	Initial	450	1.90	32	4.91	74	25.5
		400°C	850	2.61	39	2.42	108	32
		500°C	1000	2.64	40	0.53	100	34
		600°C	1050	2.74	40	0.50	104	34
	Sample with high Al_2O_3/SiO_2 ratio, mostly clay	initial	430	2.58	30	1.89	90	23.5
		400°C	570	2.68	37	1.69	92	25
		500°C	600	2.56	39	0.89	95	26
		600°C	610	2.72	43	0.65	96	26
	Sample with low Al_2O_3/SiO_2 ratio, mostly clay	initial	570	2.32	43	3.72	147	48
		400°C	850	2.42	47	2.69	153	45
		500°C	1020	2.38	49	1.87	170	45
		600°C	1015	2.44	53	1.51	165	44
	Sample with low Al_2O_3/SiO_2 ratio, containing opal	initial	870	2.38	37	2.84	126	36
		400°C	950	2.5	46	1.6	130	37.5
		500°C	875	2.38	45	1.51	128	35.5
		600°C	920	2.38	47	1.36	127	37

The processes occurring upon the heating can be summarized as follows: the gradual dehydration of clay minerals and alteration of their structure leads to the increase in porosity and the appearance of defects. Despite of observed increase in surface area, thermal treatment resulted in a shift of particle size maxima towards more coarse particles, possibly due to agglomeration and pyroplastic reactions (as demonstrated by Fig.1). Here, the excess of internal energy of the system from the dehydration of layered aluminosilicate leads to the aggregation of particles. These changes of the dispersion are quite considerable for thermal treatment at 500°C and higher temperatures resulting in the material with particle range of 25-150 μm vs. the range of 1-25 μm observed for reference material. The heat treatment and restructuring of the layered aluminosilicates lead to a performance improvement of asphalt mastics. The effect of the treatment is observed in water resistance and swelling. The coefficient of water resistance of mastics based on thermally-treated clay materials is increased by 1.5–2 times (Table 3, the ratio Al_2O_3/SiO_2 = 0.14–0.25), and the swelling is reduced by 3.9–8.8 times. This becomes possible due to the transformation of clay minerals and due to higher adhesion of bitumen to mineral fillers achieved by the presence of Lewis active centers on the surface of modified fillers [3, 6].

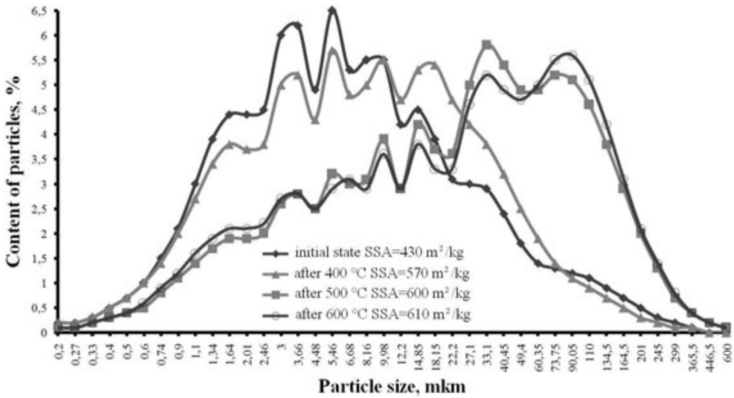

Fig.1 The effect of thermal treatment on the particle size distribution of filler with a high Al_2O_3/SiO_2 ratio, predominantly clay composition

Carbonation and burning of organic impurities in the aluminosilicate materials contribute to the destruction of aggregates and provide a significant increase of specific surface without mechanical treatment (Table 2). The considerable amount of biogenic products in the gaize (remains of diatoms) causes its high dispersion (Table 2, surface area within 870–950 m^2/kg). These materials are stable under temperature treatment and so negligible changes in the structure and dispersion of fillers are observed. The changes in the specific gravity, density, bitumen capacity are less than 27% (Table 2); water stability coefficient for asphalt binder is increased up to 15% (Table 3).

Table 3. The Water Resistance and Swelling of Asphalt Binders

Designation of sample	The coefficient of water resistance/swelling, %			
	Initial state	After 400 °C	After 500 °C	After 600 °C
Coal-bearing sample with high Al_2O_3/SiO_2 ratio (0.36)	0.9/11.2	0.92/3.52	0.91/2.76	0.92/2.67
Clay sample with high Al_2O_3/SiO_2 ratio (0.25)	0.45/18.8	0.78/10.7	0.9/2.85	0.93/2.32
Clay sample with low Al_2O_3/SiO_2 ratio (0.14)	0.61/19.4	0.88/16.4	0.94/2.83	0.95/2.19
Opal containing sample with low Al_2O_3/SiO_2 ratio (0.10)	0.83/5.86	0.87/4.62	0.94/2.95	0.96/2.57

As a result of heat treatment at 500–600 °C clay materials with various chemical and mineral compositions are formed with significant amounts of highly reactive surface centers. The results investigation of asphalt mastics with thermally treated aluminosilicate powders demonstrated an acceptable performance of the tested fillers: the water resistance in the range of 0.9–1% and swelling in the range of 2–3%, meet the requirements of State Standard (≥ 0.7% and ≤ 3.0%, respectively).

CONCLUSIONS

With the increase of activation temperatures, there is an increase of a specific surface area, porosity, bitumen capacity and the flow rate of bitumen enabling to obtain the asphalt concrete of optimal structure. The high fineness and surface morphology of the aluminosilicate fillers enables to reduce the binder content in the asphalt mixture without loss of the physical and mechanical performance.

The feasibility of application of thermally treated aluminosilicate rocks of sedimentary strata for manufacturing of fillers for asphalt concrete is experimentally established. The performance of asphalt mastics with developed fillers meets the Standard requirements.

ACKNOWLEDGMENTS

This work is supported by the Ministry of Education and Science of the Russian Federation, Grant 14.B37.21.1218, Strategic Development program of Belgorod State Technological University named after V.G. Shoukhov; Russian Foundation for Basic Research (12-08-97603).

REFERENCES

1. L.B. Gezentsvey, N.V. Gorelyshev, A.M. Boguslavskii, I.V. Korolev, *Road Asphalt Concrete*, 2nd ed. 37 p. (1985).Transport, Moscow, *in Russian.*
2. V.V. Strokova, I.V. Zhernovsky, A.O. Lutenko, M.S. Lebedev, The analysis of organo-mineral composites based on the genesis and dimensional levels of mineral raw materials. The Bulletin of the Belgorod State Technological University named after V.G. Shoukhov 4(28), (2009), *in Russian*.
3. V.V. Yadykina, E.A. Lukash, *Constr. Mater.* **11**, 46 (2009), *in Russian*.
4. L.I. Dvorkin, O.L. Dvorkin, *Building Materials Based on Industrial Wastes*, (Phoenix, Rostov-na-Donu, Russia, 2007) 173 p, *in Russian*.
5. G.I. Knigina, *Building Materials Made of Burned Rocks*. 35 p. (1966).Stroyizdat, Moscow, *in Russian*.
6. V.V. Strokova, N.I. Alfimova, V.S. Cherkasov, N.N. Shapovalov, *Constr. Mater.* **3**, 14 (2012), *in Russian*.
7. D. Georgiev, B. Bogdanov, K. Angelova, I. Markovska, Y. Hristov, *Synthetic zeolites – structure, classification, current trends in zeolite synthesis*, (Economics and Society Development on the Base of Knowledge: International Scientific Conference, Vol. 7: Technical Studies, Stara Zagora, Bulgaria, 2009).
8. C.A.R. Reyes, C.D. Williams, O.M.C. Alarcon.Synthesis of zeolite LTA from thermally treated kaolinite. Rev. Fac. Ing. Univ. Antioquia 53, Junio, 30–41 (2010).
9. S.S. Rayalu, J.S. Udhoji, S.U. Meshram, R.R. Naidu, S. Devotta. Estimation of crystallinity in fly ash-based zeolite - A using XRD and IR spectroscopy. *Curr. Sci. India.* **89**(12), 2147 (2005).
10. K.Sobolev, I. Flores, J.D.Bohler, A.Faheem, A.Covi, *Application of Fly Ash in ASHphalt Concrete: from Challenges to Opportunities,* (World of Coal Ash Conference, USA, 2013).
11. M. Arikan, K. Sobolev, T. Ertün, A. Yeginobali, and P. Türker, *Constr. Build. Mater.* **23**(1), 62–70 (2009).
12. M. Arikan, K. Sobolev, T. Ertün, A. Yeginobali, and P. Türker, *Am. Ceram. Soc. Bull.*

86(11) e9101-e9107 (2007).
13. M. Albayrak, A. Aras, M. Arikan, K. Sobolev, *Clay Miner.* **42**(2), 233–244 (2007).