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Production of Shungite Concentrates – Multifunctional Fillers for Elastomers

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Abstract
The chemical composition of shungite from "Bolshevik" deposit was studied by energy-element analysis. It was established by X-ray diffraction method that in addition to the carbon component of shungite has a mineral part: hydromica type of illite, gidromuskovit, quartz, dolomite, chlorite, pyrite and siderite. Enrichment by flotation of shungite was carried out to concentrate of carbon and stabilize composition. The possibility of partial or complete replacement of technical carbon by new fillers based on shungite in rubber mixes was studied. The influence of shungite filler on the strength properties of rubber was studied. Strength properties of rubbers filled with shungite are above, compared to the properties of rubber filled with carbon black. Reinforcing effect of elastomers filled shungite is above compared reinforcing effect of the of elastomers filled standard technical carbon black.
Key words: Shungite, Elastomer, Enrichment, Carbon, Concentrate, Filler.

Despite the fact that carbon material which is similar to the Karelian shungite was found on the territory of Kazakhstan, it continues to appear in mass media that the world's only field of shungite is in Russia, Karelia. We have been working with it for several years. In a comparative study of local carbon material ("Bolshevik" mine, East-Kazakhstan region) with Karelian shungite and several other well-known carbon materials it was confirmed that it belongs to a class of shungite. Karelian shungite themselves are very different both in structural state and on the supramolecular organization.

Shungite occur in nature as thick shungite rocks, which are densified mechanical mixtures of carbon and mineral agglomerates of various chemical composition [1,2]. Natural shungite is a multi-phase system by results of X-ray analysis (Figure 1) [3].

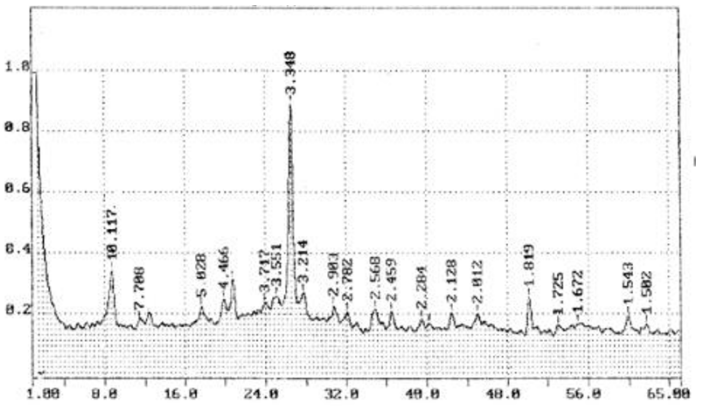

Figure 1 - Radiograph of shungite rock

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A number of mineral components were determined by characteristic diffraction peak at 10.1 A (hydromica type of illite , gidromuskovit), besides of carbonaceous material wich diagnosed by reflex with an interlayer distance d ~ 3,5 A. Diffraction reflexes of 4.26; 3.34; 1.37 A testify the presence of quartz in the rock. The diffractograms also demonstrate the presence of dolomite (3.70; 2.9; 2.012 A). Chlorite (3.53 A), pyrite (2.71; 2,41A) and siderite are present in minor amounts [4].

The given rocks are identical in qualitative composition however, are not uniform in a quantitative sense. Carbon content changes widely from a few percent to 44% by weight (Table 1). The heterogeneous composition of the mineral substrate and a wide range of changes in the amount of carbonaceous substances explain a wide variety of shungite differing appearance, physical, mechanical and chemical properties.

Table 1 - Chemical composition of shungite

No	Component content, % wt.									
Sample	C	SiO_2	TiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	Na_2O	K_2O
1	44.2	34.7	0.4	9.8	1.2	0.3	0.6	1.1	0.2	1.8
2	27.6	46.2	0.5	10.6	1.4	2.4	0.9	1.6	0.4	1.9
3	12.3	50.4	0.8	14.0	1.7	5.5	2.0	2.6	0.4	2.5
4	6.3	59.6	0.7	12.0	1.5	5.6	3.6	3.3	0.7	2.6

A necessary requirement for raw materials used in production is constancy of chemical and grain-size composition. Therefore, we carried enrichment by flotation of shungite for concentrating carbon content and stabilize composition of shungite [5, 6]. Chemical compositions of products after enrichment by flotation are presented in Table 2.

Table 2 - Average composition of products after enrichment by flotation

Products of enrichment by flotation	Component content, % wt.										
	C	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	Na_2O	K_2O	M_{Al}
Tailing	19.1	50.7	0.6	12.3	4.6	2.0	3.3	2.8	1.0	2.2	0.28
Concentrate	43.8	32.1	0.5	8.6	2.6	2.2	2.8	0.9	1.5	1.8	0.19

Then we obtained experimental batch of the shungite concentrate wich was tested for rubber mix preparation. Pilot tests of carbon concentrate were carried out on the Issyk plant of the rubber products in the workshop of rubber compounds. The formulations of standard rubber compounds used in the processes of the enterprise were taken as a basis in the work.

Batch of the rubber mixes, curing and subsequent study of the physical and mechanical properties of the finished experimental rubbers were performed in accordance with current technological reglaments and methodics of enterprises.

Thus, 120 kg of rubber mix based on Kazakhstan shungite was obtained. Rubber irrigation pipes and insulating mats were vulcanized as the products.

The elastic-strength characteristics of experimental products and products based on standard mix are given in Table 3 [7]. According to these data, physical and mechanical properties of the experimental rubbers substantially above those for the products prepared by the standard formulation (i.e. only filled with carbon black mark P 324), and meet the requirements of GOST 126.

Table 3 - Physical and mechanical properties of rubber dielectric rugs

Characteristics	Rubber rugs			
	experimental		standart	
	upper mix	plantaris mix	upper mix	upper mix
Rupture strength, MPa	7.84	9.33	7.84	7.35
Relative elongation at rupture, %	520	320	300	300
Relative residual elongation, %	19	21	25	40

CPCMRA al-Farabi KazNU has implemented the project of pilot plant construction for the production of carbon materials based on shungite rocks up to 4 million tons per year [8] in the framework of commercialization of research projects supported by the Ministry of Education and Science of Kazakhstan, the World Bank and the Scientific and Technological Center "Parasat". Finely Dispersed Shungite Concentrates (FDSP) with 40 ± 2% of carbon were obtained. Purpose of finely dispersed powders is to be used as a filler of elastomers in rubber and polymers industry [9].

Work on the shungite powders implementation [10] on rubber industries has been going on for a number of years. Powders obtained by different technologies of grinding do not differ in constancy of composition and dispersion. Table 2 presents the main properties of a commercially available FDSP produced by CPCMRA KazNU.

Table 4 - Properties of FDSP

Indicator name	Norm
1. Appearance	Finely dispersed black powder without impurities.
2. The mass fraction of carbon (%), not less than	35.0± 2.0
3. Mass fraction of losses at 105°C (%,) no more than	1.5
4. Cinder content (%), no more than	60.0
5. Packed density, g/dm^3	350-450
6.pH of aqueous extract	6.5-7.0
7. Mass fraction of residue,%, after sieving through a sieve with a mesh 0.14 0.045 no more than	 none 0.05
8. Dibutyl phthalate absorption, cm^3 / 100g	32
9. Specific adsorption surface	23

In spite of the fact that developed standard of the Customs Union (Active carbonaceous filler of elastomers - ST TOO 111040004929-04-2015) for manufactured products contains a limited list of standardized indicators, it remains a good basis for the widespread commercial introduction of FDSP in the rubber industry as a filler of polymers.

In the manufacture of rubber compounds filled with technical carbon in combination with active types of FDSP concentrates show properties of technologically active additives. Thus, they accelerate the implementation, distribution and dispersion of fillers, reduce "dusting", increase the ductility and fluidity of elastomeric composites, increase adhesion to metals, reduce the phenomenon of dangling mixture over the roll gap of rubber compositions during their processing on a roller equipment and generally improve performance of millability, the surface quality of the extruded and calendered workpieces. Therefore, the

introduction of significant FDSP dosage when used as filler either improves the "processability" parameters of rubber mixes or remains at a level of ethalon.

The obtained data of the effect of high carbon shungite powders on the structure and properties of the elastomeric composites show that FDSP is a perspective component of the rubber mixes with multifunctional actions. It combines properties of the new "diphilic" filler, plasticizer and structural technologically active additives. Certain shungite stocks with more than 30 million tons in each mine are leading to perspective industrial use along with a different stable grades of carbon blacks.

Conclusion

1 Researches shown that shungite can be used as reinforcing filler of the elastoplastic composite materials.

2. Strength properties of rubbers filled with shungite are above, compared to the properties of rubber filled with carbon black.

3. Reinforcing effect of elastomers filled shungite is above compared reinforcing effect of the of elastomers filled standard technical carbon black.

References

1. Kwiecinska B., Pusz S., Krzesinska M., Pilawa B. Physical properties of shungite // International Journal of Coal Geology. – (71). – 2007. – P. 455-461.

2. Efremov S.A. Manufacturing of carbon-mineral materials based on shungite rocks. - Diss. doc.chem.sciences: 05.17.01. – 2010. – Almaty. – 240 p.

3. Kovalevski V.V., Peter R. Buseck, Cowley J.M. Comparison of carbon in shungite rocks to other natural carbons: An X-ray and TEM study // Carbon. - (39). – 2001. P. 243–256.

4. Andrew T. Fisher, Michael B. Underwood Calibration of an x-ray diffraction method to determine relative mineral abundances in bulk powders using matrix singular value decomposition: a test from the barbados accretionary complex // Proceedings of the Ocean Drilling Program, Initial Reports. – 1995. – Vol. 156.

5. Efremov S.A., Nechipurenko S.V., Kazankapova M.K., Washington B., Tassibekov Kh.S., Nauryzbaev M.K. Physico-Chemical Characteristics of Shungite Rock of Kazakhstan // Eurasian Chemico-Technological Journal. – 2013. – №3 (15). – P. 241-249.

6. Yefremova S.V., Korolev Yu.M., Nauryzbayev M.K., Yefremov S.A. The structure of Kazakhstan shungite // Solid Fuel Chemistry. – 2003. – № 1. – P. 11–20.

7. M.Eng. Chaiyaporn Lothongkam Dielectric strength behaviour and mechanical properties of transparent insulation materials suitable to optical monitoring of partial discharges // Berlin. – 2014. – P.157.

8. Nauryzbayev M.K., Yefremov S.A., Nechipurenko S.V. The filler for the production of elastomers. Innovative patent №27326, 16.09.2013, bul. #9.

9. Zaimova D, Bayraktar E.b, Katundi D., Dishovsky N. Elastomeric matrix composites: effect of processing conditions on the physical, mechanical and viscoelastic properties // Journal of achievements in materials and manufacturing engineering. – №2 (50). – 2012. – P. 81-91.

10. Grishin B.S., Kalinin Yu.K. SRW «Finely Dispersed Shungite Powders - Promising Filler of Multifunctional Action for Elastomer Composites». – Moscow, Petrozavodsk, 2005.