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Preparation of the Silica-Reactive Filler Material

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Abstract: The article describes the main theoretical aspects of the changes of reactivity particulate materials of different origin as a result of dispersion in different mills. Some changes in the degree of crushing and concentration of the active adsorption sites of the silica-containing raw materials from time to time in various grinding mills were studied the variation of the surface properties of shredded materials using infrared spectroscopy was also studied. The paper finalizes the modernization of evaluating the performance of milling equipment, which allows to take into account the influence of the type of mill, the nature of the material, milling time individually and in their totality. From these grinding machines the best in terms of increasing the activity of the fillers of different materials was determined the contradiction, consisting in the fact that in case of increasing fineness, the number of active sites increases to a certain value of the specific surface was disclosed; then the activation process slows down considerably, which is of practical interest from the point of view of reducing energy consumption in the preparation of reactive fine fillers.

Key words: Mill · The concentration of active sites · The specific surface area · Silica-containing raw materials · The reactivity

INTRODUCTION

Creating a road network capable of meeting the high demands of our time, has a decisive influence on the pace of socio-economic development of any country. To date, the volume of traffic, including heavy trucks and trucks with an axle load to 10-13 tones have considerebly nicreased. In this capacity resources for road construction materials remained at the same level.

In order to reduce the cost of road construction has been the tendency to use different industrial wastes as raw materials for the production of road-building materials has been outlined. This in turn had an effect on the quality of asphalt pavement.

One way to improve performance is to use asphalt quality mineral powders. The traditional technology uses carbonate mineral powders produced by grinding in ball tube mills. They are in short supply in many regions of the country.

The use of unconventional materials, including silica-containing will allow to expand the range of raw materials used as filler for asphalt. However, the available raw materials often do not meet regulatory requirements, forcing the use of various technologies of its treatment, which could improve the performance of finished products. One way of implementing this objective is to make particulate material or structural instability activity. This is possible through the control of raw materials production processes, for example, by grinding, which is accompanied by mechanical activation.

MATERIALS AND METHODS

Determination of the specific surface area of the investigated fillers was performed in two ways: air permeability|-by using the Tovarova device and low-temperature nitrogen adsorption-the BET equation using the Sorbi device.

The number of active acid sites on the surface of the filler was determined titrimetrically in terms of exchange capacity with respect to calcium ions. The test was performed as described in [1].

For the test the 20 g sample of material was placed in a conical flask, at was also filled to with 20 ml of a saturated solution of $Ca(OH)_2$. The resulting suspension was stirred in a shaking table for 2 hours; after that the solution was analytically separated from the mineral material; a solution of the indicator was added into the

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resulting aqueous extracts and it was titrated with hydrochloric acid. The difference in volumes of acid used for titration of saturated solution of $Ca(OH)_2$ and the solution after reaction with a mineral material shows the degree of surface activity.

The processing of the results was performed by the following formula, micro-equivalents/ gram (mc-eq/g):

$$\frac{(V_1 - V_2) \cdot 0{,}1 \cdot 1000}{m}, \quad (1)$$

where V_1-the amount of acid is not eligible for the titration of 20 ml of the stock solution $Ca(OH)_2$ ("idle" experience), ml; V_2-the amount of acid is not eligible for the titration of the solution after the interaction with the mineral material, ml; m-sample weight of mineral material, g.

The study of phase-structural changes occurring in the grinding of the powder and then in the course of its subsequent storage under various conditions was performed using infrared spectroscopy according to the method [2]. For the test materials samples of the materials were prepared in the form of tablets based on potassium bromide (KBr). Spectrally pure KBr was pre-calcined at the temperature of 350-400°C for 3-5 hours. The test powder and potassium bromide were weighed on an analytical balance with accuracy of 0.0001 g of 250 and 2.5 mg, respectively.

The weighted components were averaged to obtain a homogeneous powder. The pressing of tablets was carried out in the press at under pressure of 18-19 MPa and with maintaining 45-50. Under high pressure KBr crystal grains become plastic and form a transparent matrix in the process of flow, in which the powder is evenly distributed of the test material.

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The production of many modern building materials is impossible without the use of highly efficient equipment for crushing materials. At present various grinding machines for mineral powders of different dispersion have been developed and applied.

We studied the following mills:

- The type of laboratory capacity up to 5 kg/h: ball, ball planetary, vibrating, vibrating eraser;
- Industrial type with capacity from 50 to 150 kg/h ball, counter-jet mill and centrifugal grinding-mixing unit.

The process of grinding in a ball mill and a vibratory mill is identical; this is abrading and impact effect on the processed material. In a vibratory milled material grains are crushed to a greater extent compared with a ball mill. The nature of the impact of grinding media for dispersible materials when grinding in a planetary ball mill is abrasive, percussion, mixed and crushing. However, the forces acting the material to be ground in planetary mills, ten times higher than the impact force on a solid body in the traditional milling equipment. In a centrifugal ball mill mineral particles are crushed under the influence of abrasion and crushing part. The principle of crushing mineral grains in a jet mill is based on its high-speed free kick on the fixed obstacles. Abracing effect of particles moving in a stream, though very intense, but very fleeting.

The objects of the study were dispersed materials from industrial wastes of the Kursk magnetic anomaly: quartz sandstone, wastes of wet magnetic separation of ferruginous quartzite (WMS), as the most promising ones in terms of the use of local raw materials. For comparison-quartz sand and crushing of granite screenings. Grain composition of the raw materials is presented in Table 1.

Samples of the above materials were milled for 5 hours in the different mills under study. In view of the fact that in addition to dispersing with mechanical a significant increase in concentration of the active adsorption sites, occurs, the important task is to define the grinding unit, in which the inorganic powder having the highest surface activity can be obtained by. For this purpose, the dependence of concentration of active Bronsted centers on the specific surface of powders, milled in different mills was studied (Table 2-3).

Based on the presented data (Table 2-3) it is clear that the highest concentration of active adsorption centers may be prepared by dispersing mineral materials in a planetary ball mills and jet counter, the lowest one by grinding in a vibrating attritor and a ball mill of laboratory and industrial types.

Due to the fact that during the machining processor the accumulation of energy in the grinding material takes place, which in turn leads to rupture bonds and the formation of free hydroxyl groups because of the adsorption of water molecules fragments, the number of active adsorption sites will depend on the machining conditions such as exposure method of grinding bodies on the material to be ground, the intensity, duration of mechanical treatment. In this case has a different mechanism for creating stresses in the grinding of various devices is of decisive importance [3-5].

Table 1: Characteristics of the grain composition of raw materials

	Complete the remains on the sieve,%				
Mineral material	1,25	0,63	0,315	0,14	less than 0.14
Quartz sandstone	0,8	12,7	30,4	74,5	99,9
Waste WMS	0,1	3,4	21,6	65,3	99,9
Granite	0,6	12,6	28,1	71,2	99,9
Quartz sand	0,4	4,9	35,3	84,1	99,9

Table 2: The dependence of the specific surface area materials of the time of grinding in mills of different

Sorted material	The specific surface, m^2/kg								
Planetary ball mill									
Grinding time, h	0	1	2	3	4	5			
Granite	20	300	440	540	595	605			
Quartz sand	30	170	332	465	551	566			
Waste WMS	70	420	589	680	716	724			
Quartz sandstone	40	350	538	635	692	700			
Vibrating mill									
Grinding time, h	0	1	2	3	4	5			
Granite	20	189	320	380	430	435			
Quartz sand	30	150	250	323	374	385			
Waste WMS	70	250	380	483	520	527			
Quartz sandstone	40	210	350	440	480	485			
Vibrating eraser									
Grinding time, h	0	1	2	3	4	5			
Granite	20	241	370	400	410	415			
Quartz sand	30	203	260	280	290	295			
Waste WMS	70	323	469	500	504	510			
Quartz sandstone	40	282	420	453	457	457			
The ball mill laboratory type									
Grinding time, h	0	1	2	3	4	5	6	7	8
Granite	20	218	284	344	375	400	420	437	445
Quartz sand	30	158	220	270	296	320	344	354	360
Waste WMS	70	258	355	412	458	496	523	536	542
Quartz sandstone	40	244	327	387	432	457	478	490	495
Centrifugal grinding-mixing unit									
Grinding time, h	0	0,5	1	1,5	2	2,5			
Granite	20	263	469	569	617	643			
Quartz sand	30	190	380	488	543	569			
Quartz sandstone	40	312	556	668	707	720			
Waste WMS	70	357	643	745	778	790			
Ball mill is an industrial type									
Grinding time, h	0	1	2	3	4	5	6		
Granite	20	190	320	390	432	464	480		
Quartz sand	30	149	253	323	365	387	406		
Quartz sandstone	40	250	413	493	540	563	570		
Waste WMS	70	314	493	570	611	614	614		
Counter-jet mill									
The frequency of the rotation starter, rev/min	0	100	500	1000	2000	3000			
The specific surface area, m^2/kg	40	222	391	512	600	663			
Productivity, kg/h	20	30	40	46	48	50			

Table 3: The dependence of the concentration of the active adsorption sites on the time of grinding in different mills

Sorted material	The concentration of the active adsorption sites, mc-eq/g								
Planetary ball mill									
Grinding time, h	0	1	2	3	4	5			
Granite	24	48	55	59	60	60			
Quartz sand	13	26	38	45	46	46			
Waste WMS	29	71	78	79	79	79			
Quartz sandstone	27	60	67	69	70	70			
Vibrating mill									
Grinding time, h	0	1	2	3	4	5			
Granite	24	34	41	44	46	46			
Quartz sand	13	21	28	30	31	31			
Waste WMS	29	52	62	64	65	65			
Quartz sandstone	27	44	52	57	58	58			
Vibrating eraser									
Grinding time, h	0	1	2	3	4	5			
Granite	24	32	36	37	38	38			
Quartz sand	13	20	22	23	23	23			
Waste WMS	29	51	53	54	54	54			
Quartz sandstone	27	46	50	51	51	51			
The ball mill laboratory type									
Grinding time, h	0	1	2	3	4	5	6	7	8
Granite	24	39	44	45	46	46	46	46	46
Quartz sand	13	23	26	28	29	30	30	30	30
Waste WMS	29	45	51	52	52	51	51	51	50
Quartz sandstone	27	45	50	50,5	51	51	50	50	49
Centrifugal grinding-mixing unit									
Grinding time, h	0	0,5	1	1,5	2	2,5			
Granite	24	40	49	52	53	53			
Quartz sand	13	25	33	34	35	35			
Quartz sandstone	27	52	62	64	65	65			
Waste WMS	29	59	67	69	69	69			
Ball mill is an industrial type									
Grinding time, h	0	1	2	3	4	5	6		
Granite	24	37	40	41	42	42	42		
Quartz sand	13	25	30	31	32	32	32		
Quartz sandstone	27	48	51	52	53	53	53		
Waste WMS	29	54	58	59	59	59	59		
Counter-jet mill									
The frequency of the rotation starter, rev/min	0	100	500	1000	2000	3000			
Granite	24	39	50	52	53	53			
Quartz sand	13	28	38	42	42	42			
Quartz sandstone	27	46	58	62	64	65			
Waste WMS	29	50	65	70	71	71			

A high concentration of proton centers is formed on the surface of siliceous powder activated by shock voltage (in a jet mill and a planetary ball). It reaches a specific surface, for example, in case of milling WMS wastes. It is equal to 400 m^2/kg of values of 65 and 73 mc-eq/g respectively. At the same time the concentration of active centres on the surface of the mineral powders of comparable fineness milled in an attritor and a vibrating ball mill is 55 mc-eq/g.

Thus, the maximum value of concentration of active centers of test materials is formed on the surface of waste WMS in grinding in a planetary ball mill (79 mc-eq/g), the minimum one on the surface of the quartz sand in the vibratory milled eraser (23 mc-eq/g).

In view of the above, it was found that depending on the exposure process of grinding bodies on the material to be ground, a change in the surface properties of particles of raw components, namely, the specific surface area, the concentration of active adsorption centers on the surface, was observed.

Besides, it is known [6-8] that the surface of ground particles acts as a specific barrier before which the dislocations moving under the influence of deformations and stress originated during grinding are accumulated; moreover, some cracks are localized in the surface layer of particles. As a result, the quartz crystal lattice is distorted, there is a "amorphization" of the surface layer of particles under grinding.

From the work [9] it is known that the mechanical processing of sand in a disintegrator improves its interaction with the bitumen and allows its use as a filler in asphalt concrete mixtures. During grinding of quartz sand local stress concentration pockets, on its surface are created partial amorphization of the surface occurs. This explains the improvement of adhesion of the film of bitumen to the activated particles of sand.

There is still no consensus on the question of whether the change comes before the actual primary crystallites or only microcrystals are formed; they like the amorphous phase, do not give any diffraction peaks in the X-ray. Therefore, the amorphous part of the quartz in the various papers is described a by number of ways in accordance with the concept of its structure, such as the phase formed by microcrystals, as a distorted crystal lattice, as a product of the destruction of the lattice of the disordered or amorphous phase [10]. It is also widely accepted to characterize this phase using the strategy for research, such as X-ray amorphous.

The study of features of the infrared spectroscopy (Figure 1) by the example of fine powders, the grinding of which was performed in a planetary ball mill showed that the local structure of the silicon-oxygen structural motif silica-containing raw materials undergoes significant changes with increasing time of dispersion. In particular, the absorption band profile is clearly fixed within the range of 800-1200 cm^{-1}. This high shear shoulder profile in the direction of decreasing wave number may indicate a

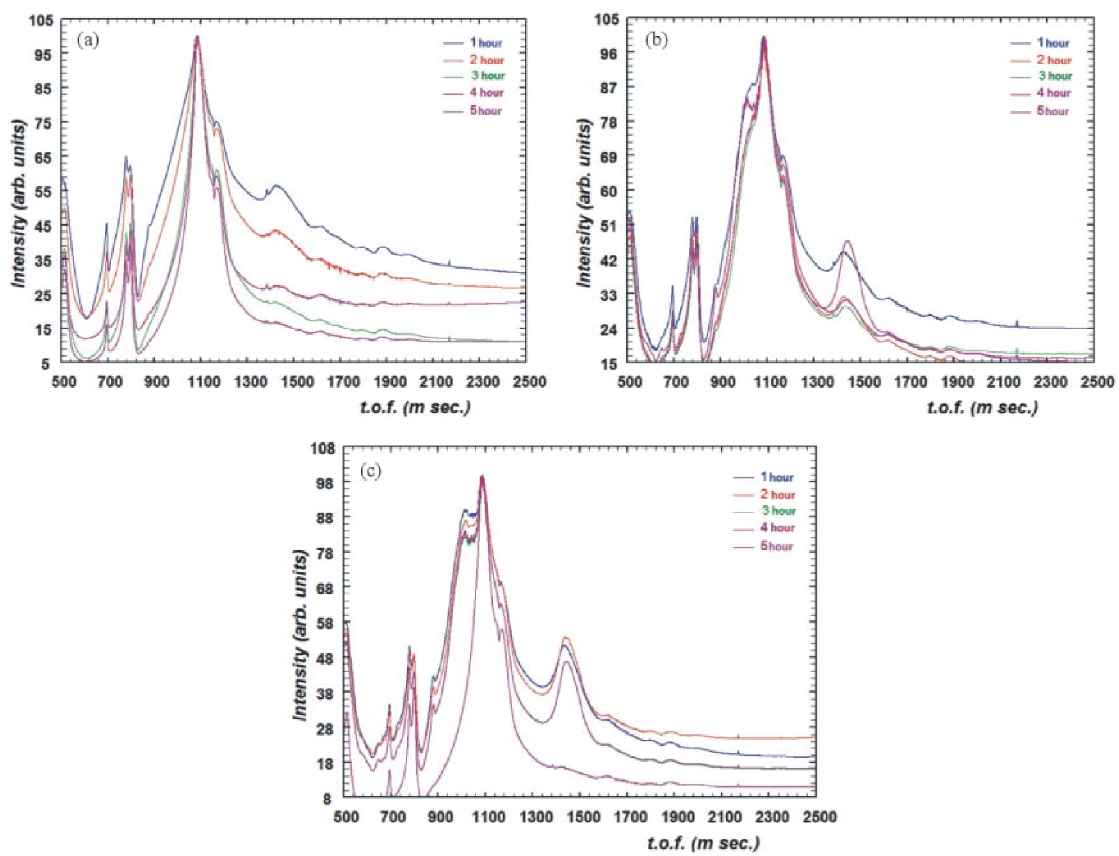

Fig. 1: Infrared spectra quartz sand (a), quartz sandstone (b) and Waste WMS (c), milled in a planetary ball mill

decrease in the number of local centers framing. This fact is in direct response to the current understanding of the mechanical activation of quartz materials.

In accordance with the experimental data on the scattering of X-rays at high angles to the mechanically activated powders of silica-containing raw materials, produced amorphous phases still contain the areas of crystalline structure. The change in structure with the formation of X-ray amorphous phase on the surface of the crushed material should also have some impact on the process of interaction in the "mineral powder-bitumen" and physics-mechanical properties asphalt cement and asphalt.

CONCLUSIONS

Thus, during the grinding process of various silica-containing material in different the grinding equipment a change of the specific surface structure value and the local structure occurs; the increase in the concentration of surface active adsorption centers that determines reactivity fillers in the production of composites construction and can affect the quality of the building material such as asphalt.

RESULTS

The analysis of the grinding equipment has shown that a planetary ball mill and a ounter-jet; they mill have the highest activation ability implement the principle of crushing impact. As a result of grinding, proton concentration increases in the range of 4.4 to 2.1 in them; the lowest one with lower a vibration eraser and a ball mill. The increase in the grinding activity in them is 2.4-1.6. In view of the materials studied the maximum value of the concentration of active centers is reached on the surface of the grinding waste WMS in a planetary ball mill (79 mc-eq/g), the minimum-quartz sand, crushed in a vibratory eraser (23 mc-eq/g).

The effect of the method of influence of grinding media on the shape and nature of the surface of the ground particles was identified. Particles of the mineral powder produced by grinding the raw material in a vibratory ball mill, attritor are characterized by proper cuboid shape and nasty surface. In this case, the primary mode of action of grinding bodies on the ground material in these mills is abrasive. The grinding of mineral material in a planetary ball, vibratory and jet mills occurs under the influence of shock loads and lead to the formation of particles, characterized by fragmentation irregular shape and rough surface pronounced.

The results obtained by infrared spectroscopy shows that the local structure of the silicon-oxygen structural motif of silica-containing raw materials undergoes significant changes with the increase in time dispersion in different grinding units. This in turn affects the reactivity of the mineral powders and may have an impact on the interaction in the system of "filler-binder."

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