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CARBONATE MINERAL POWDERS - PROBLEMS AND SOLUTIONS

Jivko Mateev
University of Mining and Geology
"St. Ivan Rilski"
Sofia 1700, Bulgaria

Nikolay Hristov
University of Mining and Geology
"St. Ivan Rilski"
Sofia 1700, Bulgaria
nhristov@mgu.bg

Dimitar Mochev
University of Mining and Geology
"St. Ivan Rilski"
Sofia 1700, Bulgaria

Lubomir Kuzev
University of Mining and Geology
"St. Ivan Rilski"
Sofia 1700, Bulgaria
lkuzev@mgu.bg

ABSTRACT
Carbonate mineral powders are obtained by grinding of several terrestrial occurrence minerals - limestones, marbles, dolomites, chalk. Fine milling in ordinary ball mils is practically impossible without adding of surfactants, which are not always safe. The process of fine milling is violated of aggregation of particles and particles sticking to the surface of the working bodies as well as surface of the working chamber of the mill. An investigation for fine milling of dolomitezed limestones from the area of village Balsha in vibratory mills with horizontally placed working chambers was carried out. Suitable working medias and regimes without adding of surfactants were defined for the production of fine carbonate powder under normal conditions.

INTRODUCTION

Carbonate rocks are terrestrial occurrence in the nature. They are used as basic building material for centuries. Currently carbonate minerals on base of $CaCO_3$ as limestone, marble, chalk, dolomite and different transitions between them found wide application in the metallurgy chemical industry, agriculture, sugar industry, buildings, glass industry, ecology and so on.

Marketing investigations and the practice shows that market demand of carbonate powders are high. It is used in different industries according to particles' size mainly as a filler:

- in the paper industry with size up to several microns;
- in the production of plastics (after modification with reagens)
- in the tire and rubber industry;
- in the pharmaceutics industry;
- in asphalt mixtures for tarmac road constructions.

The main requirements of the customers are in two directions:

- Granulometric content of the product;
- Minimal content of impurities;

Requirements for the granulometric composition are satisfied by the processes of milling, crushing, sieving and classification. Technological flowsheets and the specific apparatus define the final price of the product. Decreasing the size of the particles cause difficulties not only to the process of grinding but also in the processes of classification and sieving.

TECHNOLOGICAL BASES

Carbonate powder used for production of tarmac road mixtures for road constructions according to BDS should fit the following conditions for granulometric composition given in Table 1.

Table 1.

Index	Value, %
Granulometric content , %	
Particles passed trough sieve 1,25 mm	100
Particles passed trough sieve 0,315 mm	> 90
Particles passed trough sieve 0,071 mm	> 70
Moisture, %	< 1

Changes in the economic conditions in Bulgaria and applying the world standards in the area of road building change the requirements given in Table 1.

Road construction managed by foreign firms require applying of different standards, to guarantee better quality of the road coverings.

Mineral powder as an ingredient of tarmac road mixtures consist of fine particles obtained from milled limestones. It should be well dried. It should not contain lumps and should fit the requirements AASHTO T 37 given in Table 2.

Table 2.

Index	Value, %
Granulometric content, %	
Particles passed trough sieve 0,6 mm	100
Particles passed trough sieve 0,15 mm	85
Particles passed trough sieve 0,075 mm	75

Activated mineral powder is very often used as mineral filler in the tarmac road mixtures. It is made by milling of carbonate minerals and modification with activated mixture of bitumen and surfactants.

Activated mineral powder should fit the requirements for hidrophobicity and to be homogeneous. It should not get compressed with drying and should fit the granulometric composition defined by AASXTO T 37 given in Table 3.

Table 3.

Index	Value, %
Granulometric content, %	
Particles passed trough sieve 0,6 mm	100
Particles passed trough sieve 0,15 mm	90
Particles passed trough sieve 0,075 mm	80

The referred as illustration standards are not only ones used at the moment but the others foreign standards also have strict requirements to the granulometric characteristics of the carbonate fillers applied in the tarmac road mixtures. Obviously the Bulgarian manufacturers should take into consideration new realities to answer on the increased requirements.

"Ljuliacite" deposit characteristic

Ljuliacite deposit is situated in the south slopes of "Stara Planina" about 7 km near the village Balsha, Sofia region. It has occupied area “Kamiko” and “Machnov vrah” and lands on the north and east-north. The rocks comprise Jura and Triassic sediments. Middle and bottom Treas as well as upper Jura are represented. Two units are formed in the deposit region.

- Carbonate one comprises compact limestones, dolomitized limestones and limestonized dolomites.
- Limestone-mergel one comprises mergels, alevrite limestones and limestones.

Limestones as well as dolomites are rarely in pure form.

As percentage the distribution has the following description:

Limestones -	39%
Dolomitized limestones -	42,7%
Limestonized dolomites -	11%
Dolomites -	1,8%
Limestonized mergels -	5,3%

MDZ “Balsha” produces classes of crushed stone for the building purposes. The offered classes are 0 – 4 mm, 4 – 8 mm, 8 – 12 mm, 12 – 16 mm, 16 – 20 mm, 20 – 32 mm. A powder like product is collected from the aspiration of the working crusher and sieved equipment.

Despite that this powder product does not fit the requirements even of the BDS but it is successfully sold as mineral carbonate powder. This fact shows the existing lack of carbonate powders – fillers.

METHODOLOGY AND EQUIPMENT

The methodology for defining of suitable conditions for fine milling of carbonate rocks being treated in MDZ “Balsha” under the laboratory conditions in vibratory mill with horizontally placed working chamber include the following moments:

- Defining of the optimal quantity of material for milling in interrupted regime with one working media;
- Defining of optimal duration of milling with constant quantity of the milled material;
- Defining of suitable working media under optimal output of the working chamber with material.

The results of the milling are controlled by measurement of the yield of minus class 0,063 mm by dry sieving in vibratory devise.

The class of 4 - 8 mm was used for the purpose of investigation.

The chemical content of the sample defined by AES – ICP is: CaO - 54,1%, SiO_2 - 0,94%, Fe_2O_3 - 0,24%, Al_2O_3 - 0,32%, MgO - 0,34%, K_2O - 0,34%, Na_2O - 0,20%, ЗПН - 42,60%.

The sample for investigation is additionally crushed in roll crusher and the granulometric composition is shown at Figure1.

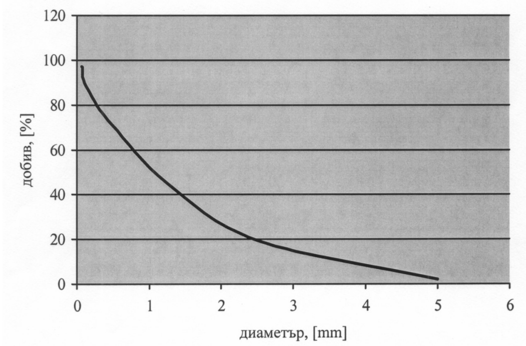

Figure 1. Granulometric content of the investigated sample.

The investigation is carried out with laboratory vibratory devise with working chambers with volume 350 cm^3. Vibratory parameters were kept constant: f – 1430 min^{-1} and A – 3,4 mm.

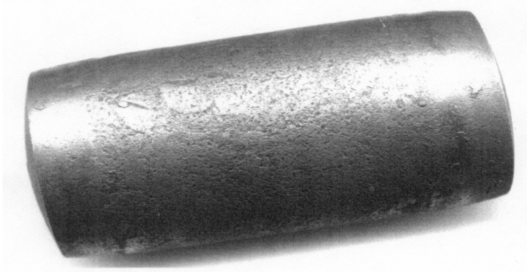

Figure 2. Working media 1 – smooth steel rod

The working medias are shown at figure 2 and Figure 3. Figure 2 shows smooth steel rod with weight of 1040 g and length 94 mm. Two working media are given at Figure 3 - smooth steel rod with weight of 155 g and length 94 mm and riffle steel rod with weight of 120 g and length 94 mm.

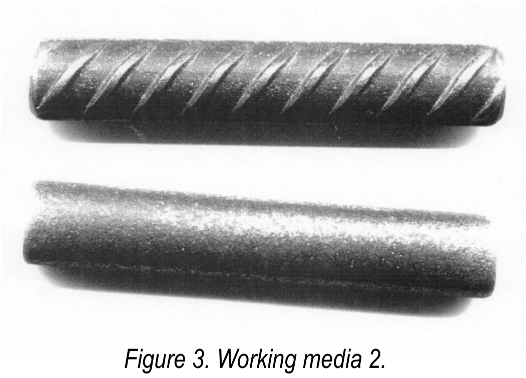

Figure 3. Working media 2.

RESULTS

The investigation for defining of the optimal quantity of the sample for milling in working volume of 350 cm^3 and working media of smooth steel rod with weight of 1040 g is carried out for the interval of 30 to 110 g with step of 20 g and duration of the milling – 3 min. The obtained results are given in Table 4.

Table 4.

Sample quantity, g	30	50	70	90	110
Observed class, (-0,063 mm),%	10,34	13,00	22,86	21,82	18,89

The investigation for defining of optimal milling duration with quality of the sample 70 g with smooth steel rod with weight of 1040 g gave the results shown at Table 5. The interval of 1 to 7 min. was observed.

Table 5.

Treatment duration, min	1	2	3	4	5	7
Observed class, (-0,063 mm),%	15,71	24,29	22,86	22,57	20,71	18,57

The investigation for different working media includes:

- Smooth steel rod with weight of 1040 g;
- Two smooth steel rods (weight of one rod – 155 g) and riffle rod with weight 120 g – working media 1;
- Three smooth steel rods (weight of one rod – 155 g) and riffle rod with weight 120 g – working media 2;

The investigation of the different working media shows the results:

- The results obtained by the milling with one smooth steel rod with weight of 1040 g and 70 g quantity of the sample are shown at Table 5.
- Vibration milling with milling media 1 (two smooth rod and one non-smooth) and media 2 (tree smooth rods and one riffle rod) with quantity of the milled sample 70 g is investigated in the interval 3 – 19 min. with step 2 min. Results are given in table form – Table 6.

Table 6.

Treatment duration, min	3	5	7	9	11	13	15	17	19
Working media 1									
Observed class, (-0,063 mm),%	18,57	22,86	30,0	32,86	39,29	46,43	51,43	55,0	58,57
Working media 2									
Observed class, (-0,063 mm),%	23,98	34,42	47,13	59,29	63,55	66,21	70,0	75,71	81,43

DISCUSSION

The effect of decreasing of the process efficiency after reaching definite stage of milling is known for dry milling of some mineral raw materials – carbonate rocks. An opposite process of aggregation and sticking of the fine milled particles on working bodies and the surface of the working chamber in observed. This process appears in different size of the different materials and depends on physicochemical characteristics, milling conditions, moisture and so on. Structural features of the mineral particles represent as defects, relief, sectility, crystal size, the character of the coalescence of the crystals an so on defines the character of the crystal destruction. The crystal destruction depends also on physicomechanical properties as hardness. The experiments for defining of correlation between these parameters and the size of the milled material does not lead to generally valid answer.

The existing practice of milling of carbonate rocks is multifarious. Combination of hit crusher and sieving, milling in two-chamber pipe mill with working media in the first chamber – steel balls and in the second chamber cilpebs combined with air classification are used under dry conditions.

Obtaining of high percentage (over 80 %) class – 0.074 mm is possible by stage milling and classification but the technological flowsheet become very difficult for maintaining and the obtained product expensive.

The investigation of vibration milling of carbonate rocks for obtaining of powder suitable for tarmac road mixtures for the road infrastructure is realized in vibratory mill with horizontally placed working chamber. The milling in the vibration mill is several time quicker than the milling in the ball mil but the process of aggregation and sticking of the fine milled carbonates is also quicker.

Possibilities for fine milling in vibration mills are hidden the chousing the proper milling medias. Smooth and riffle steel rods with different sizes are investigated as milling media in interrupted cycle. The obtained results of the milling represented as observed class – 0,063 mm give reasons for the following conclusions:

- Milling with smooth rods is impossible due to the aggregation of the fine carbonate particles;
- Milling with riffle rod is possible but the efficiency of the process is low;
- Milling with combination of smooth and riffle rods gives possibilities for obtaining of high efficiency of the process and reaching of the observed class over 80 % without usage of

surfactants, without sieving or classification.

This fact could be probably explained by the impact of the riffle rod expressed by the scoured effect of the riffle rod over the working surface. Probably mechanical is the impact over the smooth surface of the steel rods. This process is possible due to the features of movement of the working media in the volume of the chamber under vibrations. The morking media take part at the same time in two movements:

- Vibration and rotation movements around the long axis of the rod;
- Vibration and rotation movements of the whole working media opposite to the direction of the vibrations around the common axis passing to the length of the working media.

From practically point of view fine milling of carbonate rocks are possible by usage of combined working media. The treatment duration could be optimized. Carbonate powder suitable for tarmac road mixtures could be obtained by optimization of the treatment duration of continuous technological process without usage of additional sieving or classification.

CONCLUSION

Vibration milling of carbonate rocks in vibration mill with horizontally placed working chambers with mixed working media of smooth and riffle rods is a technological solution of the problem of aggregation and sticking of fine carbonate particles on the surface of the working chamber and working bodies. Vibration milling with combined working media simplify the technological flowsheet for production of carbonate powders because the processes of sieving and classification becomes redundant.

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