

Mechanochemical activation of natural and technogenic raw materials in the production of high strength plaster

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Abstract Currently, the growth of production of gypsum materials and products exceeds the economic growth of the world markets. More than 90% of binder manufactured of natural raw materials is produced of low grades, and, for production of high strength gypsum by crushed stone autoclaving, not more than 40% of extracted raw materials are used. This is due to low percentage of crushed stone of required fractions (larger than 30-50 mm) is produced from the rocks by crushing and classification. The accumulated industrial experience showed that further development of production of high grade gypsum binders is possible provided it is subject to a substantial reduction of technology, increase of productivity and reduction of fuel and energy consumption. A technology of production of gypsum binders of small fractions of gypsum rock and phosphogypsum by mechanochemical activation (MOSS) of raw materials is proposed and developed. Advantages of the suggested technology: 1. In production of high-strength gypsum binders the technology allows complete processing of raw materials, including fines generated during crushing (fraction smaller than 5 mm); 2. By changing the maximum grain size and application of MOSS, total time of heat processing (autoclaving and drying) is reduced by 2.5 – 3.04 h, which allows reducing fuel and energy consumption; 3. Operation of binder grinding after drying is excluded.

1. Introduction

Currently, the growth of production of gypsum materials and products exceeds the economic growth of the world markets.

More than 90% of binder manufactured of natural raw materials is produced of low grades, and, for production of high strength gypsum by crushed stone autoclaving, not more than 40% of extracted raw materials are used. This is due to low percentage of crushed stone of required fractions (larger than 30-50 mm) is produced from the rocks by crushing and classification.

For the last 5 years, the demand for high-strength gypsum binder has increased more than 2 times. This may be explained by higher requirements of producers of dry mixes to the binder, widening range of gypsum products in construction, medicine, engineering.

Technology of producing high strength plaster in liquid media economically is not effective due to high expenditures for binder drying.

In regions having no natural resources, the cost of gypsum materials and products is, as a rule, higher due to their shipping.



2. Materials and methods

Under industrial conditions, two ways of production of gypsum binders, consisting of semi-aquatic calcium sulfate are used – dry and wet. The wet method presupposes treatment of raw materials in the saturated steam environment at a temperature of above 97°C. The hydrothermal treatment produces relatively large crystals of semi-aquatic calcium sulphate (α -hemihydrate) and gypsum binders of high grades by strength (G-12 to G-25), due to a low specific surface and water demand. There are available various technologies of α -hemihydrate production. /1/

1. Water vapor is supplied from a boiler
 - 1.1 Hydrothermal treatment and drying are carried out in separate apparatuses
 - 1.2 The heat treatment is performed in a single apparatus (autoclave, damper)
2. Saturated water vapor generates during gypsum dehydration (method of gypsum calcining without external steam supply)
3. During processing dispersed industrial waste (phosphogypsum), autoclave treatment of aqueous slurry is carried out in apparatus of continuous action. /2,3/.

Despite of the high demand for gypsum binders of high grades, their share in binders production up to now has not exceeded 1%. The reason is inefficiency of available developed technologies of the wet method of production.

In case of natural gypsum stone, raw materials undergo operations of grinding and classification. After the classification, gravel fractions larger than 40 mm. are used. The output of the graded crushed stone usually does not exceed 40-50% of the mass of processed materials, depending on the phase composition of the stone, its structure and texture. The fines are either wasted or used for production of gypsum binders of grades G-2 to G-7 by the dry method (the Samara plaster plant). The disadvantages of this technology are the relatively low equipment productivity and high consumption of fuel and energy. For example, at the Samara plaster plant the total duration of heat treatment (autoclaving and drying) exceeds 10 hours. The technology includes operations of grinding and classification of raw materials, autoclaving, drying and grinding of the binder.

At autoclave processing of small fractions of raw materials (gravel, sand and dust fractions), a crystalline concretion forms in the autoclave during processing. The transformation of dihydrate to hemihydrate results in the formation of intergrowths at the contact between grains. The number of contacts and the strength of the formed structures – stone formed of hemihydrate calcium sulphate, depend on the average grain size and grain composition as a whole. /4,10,12/

The industrial processing of dispersed industrial waste (phosphogypsum) aqueous suspension is prepared, W/t may reach 1.0; an additive that modifies the rate of growth of hemihydrate crystal faces is introduced. The technology involves operations of liquid phase filtering and binder drying. The resulting hot filtrate contains dissolved substances and must be disposed. Industrial experience of production of high-strength gypsum binder (G-12, G-14) from phosphogypsum showed that the binder can not compete with similar products manufactured of natural raw materials. /2,3/

The accumulated industrial experience has shown that further development of production of high grade gypsum binders is possible provided it is subject to a substantial reduction of technology, increase of productivity and reduction of fuel and energy consumption.

3. A technology of production of gypsum binders

A technology of production of gypsum binders of small fractions of gypsum rock and phosphogypsum by mechanochemical activation (MOSS) of raw materials is proposed and developed.

Works /5,8,9/ show that it is possible to shorten significantly the technological process by carrying out plastic deformation of materials before hydrothermal treatment, and changing modes and environment of its implementation.

The authors described it under conditions of localized loads, shapes of pressure or shapes of impact appeared on crystal faces, the shape and structure of which depend on the structure of the crystal lattice.

The studies were conducted on the 1st grade gypsum stone of two Volga deposits - Bebyaevskoe and Kamskoe Ustie. Table 1 gives the chemical composition of gypsum stone samples and gypsum content.

Table 1. Chemical composition of gypsum

Deposit	Content, %						
	CaO	SO ₃	MgO	Al ₂ O ₃ +Fe ₂ O ₃	SiO ₂	H ₂ O chem.SV.	CaSO ₄ • 2H ₂ O
Bebyaevskoe	31.9	45.4	0.15	0.06	0.19	19.93	97.5
(Nizhny	–	–	–	–	–		–
Novgorod	32.30	46.6	0.71	0.59	1.50		98.5
region)							
Kamsko-	31.8	44.0	0.08	0.07	0.04	to 20.58	98.2
Ustinskoe	–	–	–	–	–		
(Republic of	32.8	46.9	0.7	0.78	0.34		
Tatarstan)							

Gypsum rocks of Bebyaevskoe and Kamsko-Ustinskoe deposits vary in structure; Bebyaevsky gypsum is medium-grained, Kamsko-Ustinsky one is fine. Compression strength of the rocks varies from 5.0 to 30 MPa.

The process of transformation of gypsum to hemihydrate calcium sulfate during hydrothermal processing may be divided into three periods. /1,6,13/

1. A preparatory latent period. During this period, conditions for subsequent transformation are created – a saturated aqueous solution of required concentration is formed.
2. A period of formation of centers of hemihydrate crystallization (embryo crystals). The crystal nuclei are formed mainly on the defects of crystal structure of the original gypsum, as it will be shown below.
3. A period of predominant crystal growth of semi-aquatic calcium sulfate and formation of crystalline intergrowths.

Figures 1 and 2 show the results of a complex thermogravimetric analysis of Bebyaevsky gypsum (DTA and TG). A sample consisting of particles smaller than 200 microns was used. Individual samples were obtained by quartering. Figure 1 shows the results of analysis of a sample without MOSS (moisture content is less than 0.1%).

The second sample was subject to distilled water dilution (W/T=0.20) and treatment on laboratory runners for 5 minutes. The sample was dried at a temperature of 450C. The results of DTA and TG are given in Figure 2. The grain structure of the sample after the MOSS is determined by a LA-300 laser analyzer of Kariba firm and is shown in Figure 3.

The DTA proved that MOSS accelerates the processes of transformation of dihydrate – hemihydrate and hemihydrate – anhydrite at heating. Endothermic effect corresponding to the dihydrate – hemihydrate transition is shifted to lower temperatures (182 and 1670C, without treatment and after MOSS respectively), the total duration of dehydration changes as well.

The shift of endothermic effects to the range of lower temperatures may be caused by the change of concentration of crystal structure defects of gypsum. In this regard, we assume that the pre-MOSS of raw materials may help reduce the hydrothermal treatment and, therefore, consumption of fuel and energy for production of gypsum binders of high grades (α -hemihydrate).

For researches, an installation for microscopic studies of crystallization of α -semi-aquatic gypsum during autoclaving was used.

The installation consists of a small vertical autoclave with an internal working volume of approximately 200 cm³, having 2 portholes of heat-resistant quartz glass in the top and bottom parts.

Visual monitoring of the processes of recrystallization in aqueous gypsum suspensions during

autoclaving showed that α -hemihydrate crystals appeared and grew at a temperature of 124 - 125 °C and pressure of 0.13 MPa, and higher temperatures and pressures of saturated vapor corresponding those temperatures.

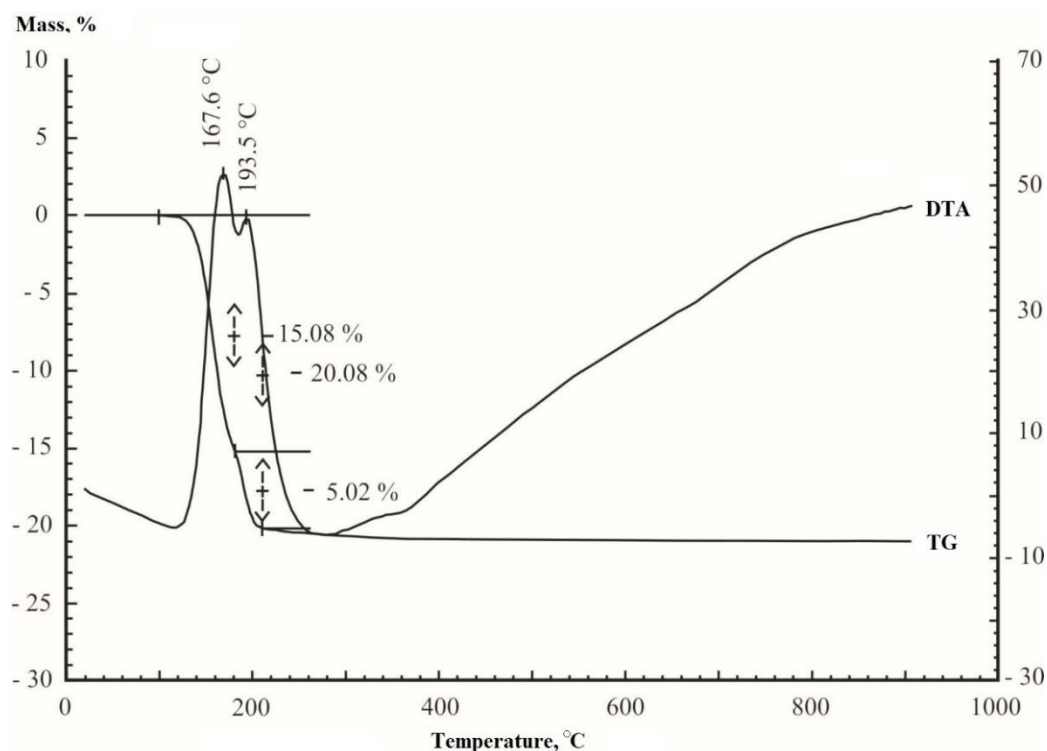


Figure 1. DTA of Bebyaevsky gypsum.

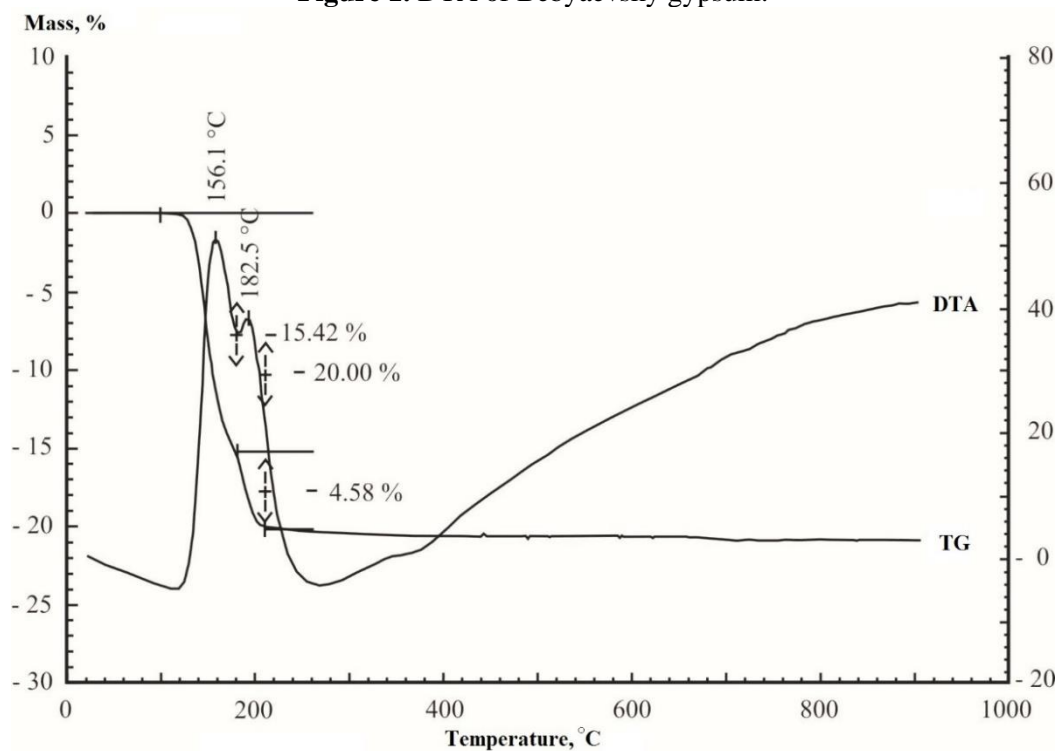


Figure 2. DTA of activated Bebyaevsky gypsum.

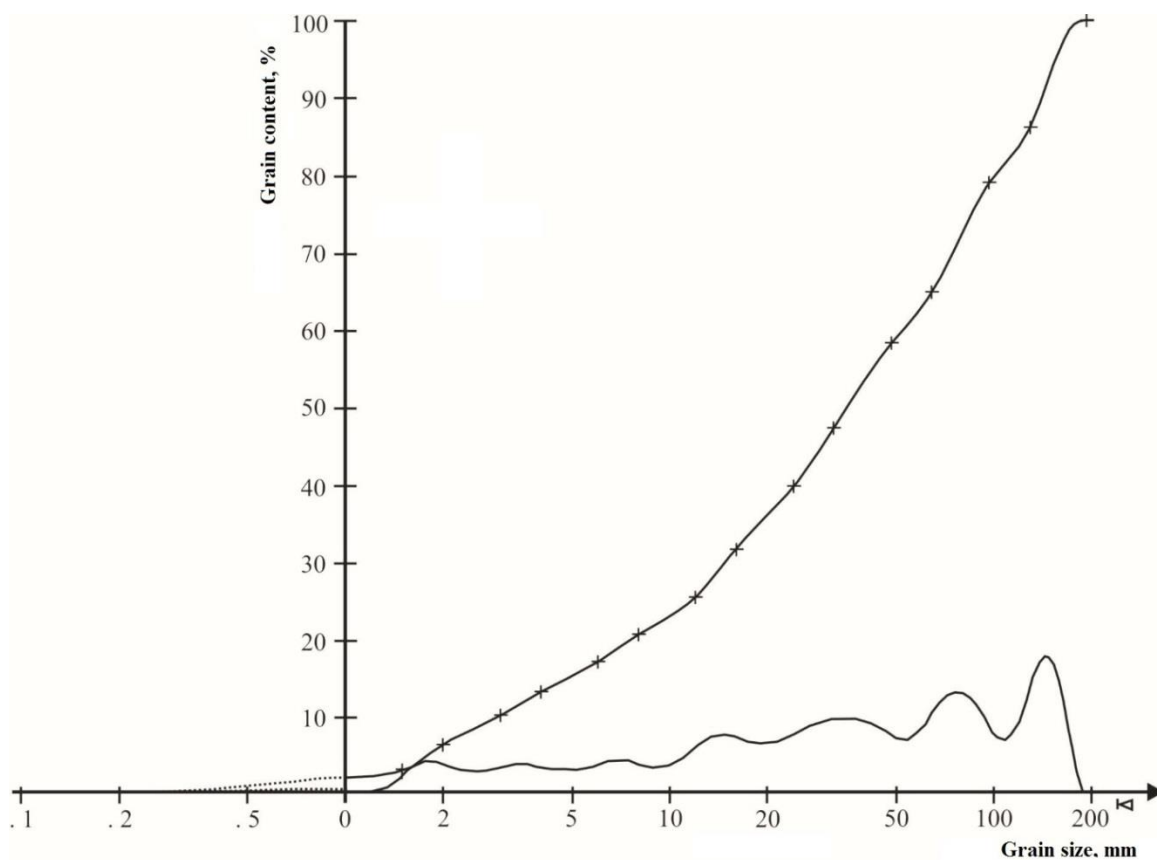


Figure 3. Grain structure of Bebyaevsky gypsum stone after MOSS.

The studies showed that the germs of hemihydrate crystals formed at the defects of the crystalline structure of gypsum (Figure 4).

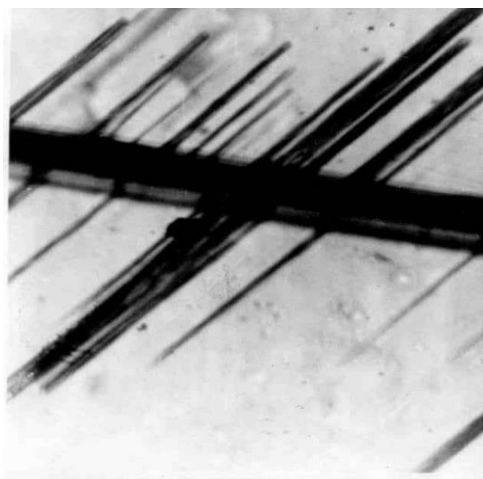


Figure 4. Crystallization of α – hemihydrate in hydrothermal conditions

At autoclave processing, α –hemihydrate crystals of non-isometric shapes (Figure 5) formed creating crystalline aggregates.



Figure 5. Crystals of α -hemihydrate obtained under hydrothermal conditions without introduction of modifying additives

It is known, that the growth rate of α – hemihydrate crystal planes and, hence, their shape can be changed by introduction of additives – modifiers [6,11,13].

We used succinic and adipic acid as modifiers. Gypsum raw material fractions smaller than 5 mm were placed in laboratory runners for MOSS. The processing was carried out for 5 min. with the flow of the aqueous solution of the modifier. W/T was taken equal to 0.20. The quantity of modifier was changed, the optimal consumption constituted 0.05% of raw gypsum mass.

The autoclave treatment was conducted at a maximum temperature of 125°C and the saturated vapor pressure 0.13 MPa. The duration of treatment was changed. The processed raw material was loaded into a container and placed into an autoclave. At the end of the process of hydrothermal treatment, drying was carried out in the autoclave without removing the container. In the result binder was obtained, which did not require additional grinding. Photomicrographs of gypsum after the MOSS and binder are given in Figures 6 and 7 respectively, the results of determination of the grain composition – in Figure 8.

The test results are shown in Table 2.

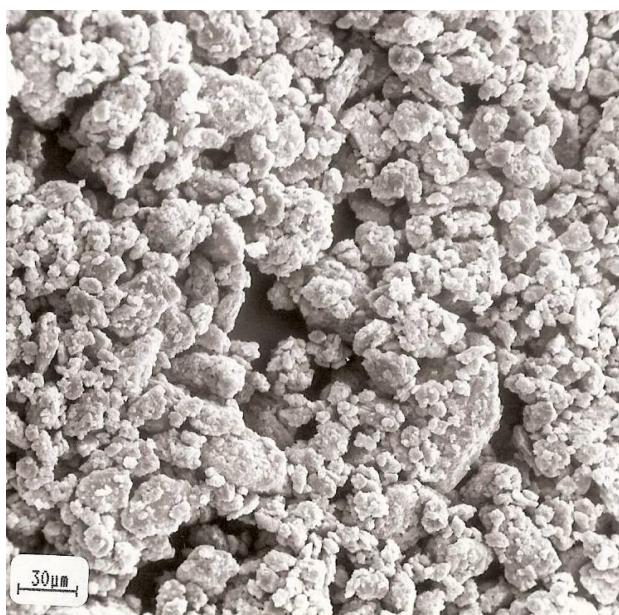


Figure 6. Gypsum of the Bebyaevskoe deposit after MOSS.
A/T=0.20, modifier – succinic acid – 0.05% of the raw material weight

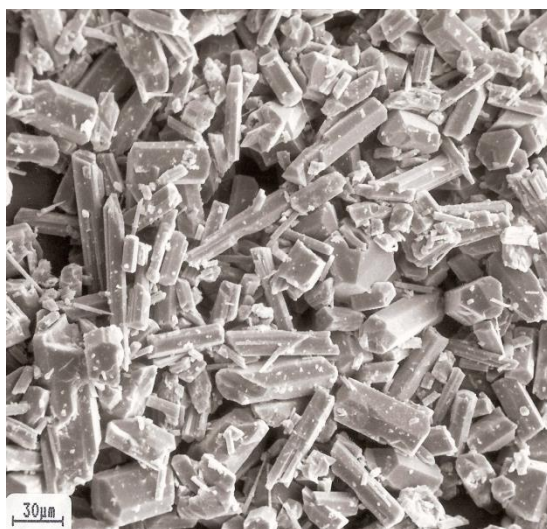


Figure 7. Gypsum binder (α -hemihydrate) after autoclaving and drying

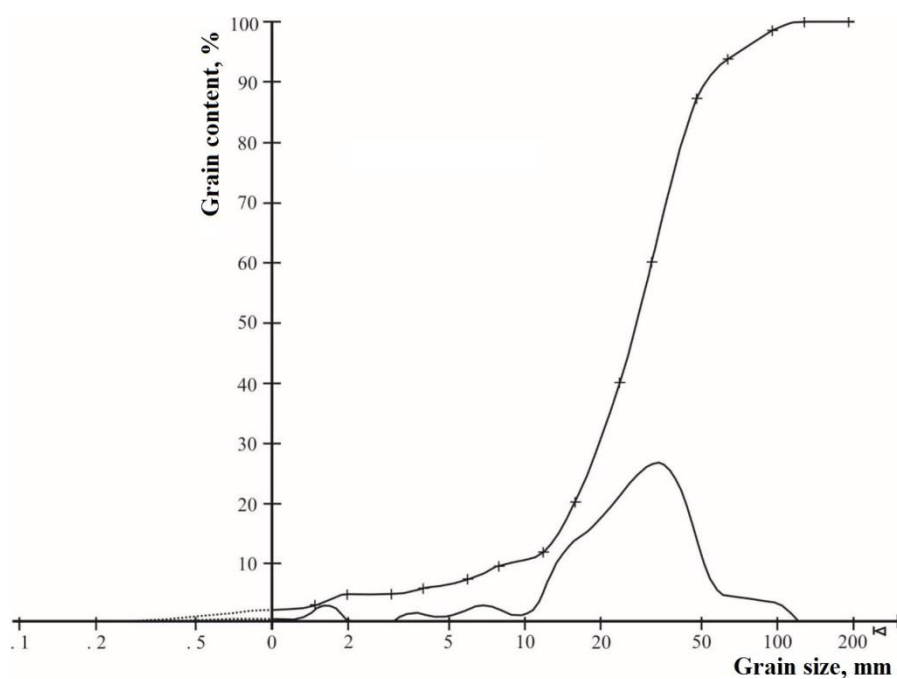


Figure 8. Grain structure of gypsum binder.

The binder, derived from activated raw materials with a maximum grain size equal to 5 mm, after MOSS and autoclaving meets the requirements of GOST 125 on grain composition.

Table 2. Technical properties of gypsum binder

The type of modifier	Water requirement, %	Setting time, min		Compression strength, MPa, at age of 2 h
		beginning	end	
Succinic acid	32	25	30	29.5
Adipic acid	42	10	12	21.5

4. Conclusion

The hydrothermal treatment of gypsum rocks of Babaevskoe and Kamsko-Ustinskoe deposits after MOSS in presence of modifiers produces high-strength gypsum binders of grades G-16 to G-25. Moreover, duration of the hydrothermal treatment is reduced from 7.0 hours (without MOSS) to 4.5 hours.

On the basis of studies conducted in laboratory and experimental-industrial conditions a technology of production of high-strength gypsum binder of natural gypsum rock is offered.

Acknowledgments

The advantages of the suggested technology:

1. In production of high-strength gypsum binders the technology allows complete processing of raw materials, including fines generated during crushing (fraction smaller than 5 mm);
2. By changing the maximum grain size and application of MOSS, total time of heat processing (autoclaving and drying) is reduced by 2.5 – 3.04 h, which allows reducing fuel and energy consumption;
3. Operation of binder grinding after drying is excluded.

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