

The hydrophobic modification of gypsum binder by peat products: physico-chemical and technological basis

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SUMMARY

Gypsum binder is a quick-setting and fast-hardening material that is used widely in the construction industry for plastering and as an ingredient of concrete, other binding materials, *etc.* The issue addressed here is its short shelf life (around three months) which arises because it is hygroscopic, *i.e.* it readily absorbs moisture and begins to set during transport and storage. The main methods that are currently available for protecting gypsum binder against unwanted exposure to moisture and water vapour are considered, and hydrophobic modification with the bitumen released during peat thermolysis (a method previously considered for cement) is proposed as a promising alternative. Because there is overlap in the temperature ranges used in the manufacture of gypsum binder and those required for the initial stages of thermal decomposition of the organic matter in peat, it is expected that hydrophobisation could be achieved during the established manufacturing process without any changes to plant or procedures. The optimum concentration of organic (peat) additive for gypsum rock mined from the Shushokskoye deposit in Russia is derived experimentally. With 0.5–1 % of peat additive, the strength grading of the gypsum plaster is preserved and its storage time without caking and hydration increases, even under adverse conditions (100 % relative humidity). The proposed method is compatible with current gypsum production technology, it does not require any changes in equipment, and the prices of mineral raw materials and semi-finished peat products are approximately the same. Thus, the incorporation of hydrophobic modification using peat into the manufacturing process for gypsum binder is unlikely to increase the cost of the product.

KEY WORDS: additive concentration, peat bitumen, sample strength, technological scheme, water repellency, water vapour absorption

INTRODUCTION

The gypsum binder (calcium sulphate hemihydrate) used in the construction industry is a quick-setting and fast-hardening mineral binding material. It is widely used for plastering, in the manufacture of gypsum concrete, building products, castings and forms, and as an additive to other binding materials. Pure calcium sulphate hemihydrate can be found only rarely in nature. Therefore, gypsum binder is manufactured (as a fine powder) from naturally occurring (mined) gypsum dihydrate, by heat treatment in the temperature range 140–190 °C.

One of the main issues that arises when using gypsum binder is the reduction in its activity that occurs over time, due to its hygroscopicity. The intensity with which it absorbs water from the atmosphere depends on the ambient temperature and humidity (Khigerovich & Baier 1979). As water is absorbed during storage, there is a gradual transformation of gypsum hemihydrate into the dihydrate, and this reduces the setting and hardening activity of the binder when it is eventually used. The

longest shelf life is considered to be three months, during which time the activity of gypsum binder reduces, on average, by 30–50 % (Gorchakov & Bazhenov 2012). Moreover, water absorption by gypsum-based building materials after application results in low frost resistance, which makes them unsuitable for exterior use unless they are additionally treated with traditional hydrophobic compounds.

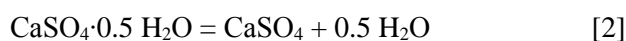
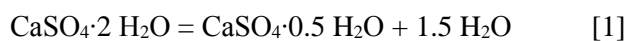
There are several established methods for protecting hygroscopic materials from exposure to moisture and water vapour. For example, they can be stored in airtight plastic containers which are kept in dry places. Other methods involve processing to apply isolating coatings to their particles or powdering them with liquid or solid flowing agents, to prevent or hinder the access of water molecules to the protected particles. In this case the protective film or flowing agent should be highly water repellent - it must possess the property of hydrophobicity.

Misnikov (2016) presented the scientific basis of a new method for hydrophobic modification of mineral binders. He applied a film coating of

bitumens released during thermal decomposition of the organic matter in peat, ideally at temperatures in the range 180–250 °C, to the particles of cement. The stage of cement processing that is most suitable for applying a hydrophobic additive is when the clinker (raw mix) is being ground in the ball mill. Joint grinding of cement components with peat will result in the application of discrete organic coatings to the mineral particles (Misnikov 2014, Misnikov & Chertkova 2014) and thus increase the hydrophobicity of the cement to some degree, but the principles described by Misnikov (2016) cannot be fully implemented in this way. Thus, it will not be possible to achieve the maximum possible effect (full isolation from moisture) until existing technological processes for the production of cement have been adapted (Gorchakov & Bazhenov 2012). On the other hand, it is likely that maximum hydrophobisation could be achieved by incorporating the method of Misnikov (2016) into established technology for the production of gypsum binders, because there is overlap between the conditions (temperature, time, presence of oxidation agents, *etc.*) imposed during the manufacture of gypsum binder and the requirements for thermochemical degradation of peat (Rakovskii *et al.* 1959, Sulman *et al.* 2009).

Industrial production of gypsum binding materials

Under normal conditions, gypsum dihydrate is a thermodynamically stable solid-phase system with minimal free energy. Figure 1 provides a full scheme and temperature ranges for the changes that it undergoes on heating (Ferronskaya 2004). The principal physical and chemical process in the production of gypsum binding materials is the disengagement of chemically bound water from the crystal lattice, according to the following chemical reactions:



The main product is gypsum hemihydrate, with the modification (α or β) depending on the magnitude and duration of the heat treatment. To enable these reactions, it is necessary first to create an environment in which moisture will be released from the gypsum dihydrate as droplets of liquid. At a later stage the gypsum will start to crystallise in large,

dense or transparent prisms or needles. Gypsum binder can be manufactured in the form of α -calcium sulphate hemihydrate by thermal exposure (at temperature (T) = 97–115 °C) of gypsum dihydrate in an aqueous medium, saturated steam, or a number of salt solutions. The alternative gypsum modification (β -calcium sulphate hemihydrate) presents the smallest aggregates of non-distinct crystals. It is formed by heating gypsum dihydrate at $T = 100$ – 160 °C under normal conditions with evaporation of moisture in the superheated steam state (Ferronskaya 2004). During this process, the structure of the particles changes and the internal surface increases¹. As the treatment temperature increases (up to 170–180 °C for β -hemihydrate, up to 200–210 °C for α -hemihydrate), the remaining crystallisation moisture is removed, producing β -dehydrated and α -dehydrated hemihydrates in accordance with the reaction mechanism shown in Equation 2 (above). In this case the dehydration does not cause any visible structural changes.

The industrial thermal treatment of gypsum dihydrate to produce gypsum binder (Figure 2) requires 1–2 hours in special boilers with constant stirring. Depending on the properties of the raw materials and the specification for the mineral binder that is being produced, the maximum temperature of the material at the time of discharge from the boiler is generally in the range 140–180 °C. The process is divided into three stages. The first stage (A–B in Figure 2) lasts about 20 minutes. During this time the temperature of the powder slowly increases from ~80 °C (temperature at charging) to 120 °C, which is the threshold for intensive dehydration of gypsum. In the second stage (B–C), the temperature is held at 120 °C for 30 minutes. This stage is characterised by intensive dehydration of the material with the removal of crystal water. In the third and final stage (C–D), duration 35–40 minutes, the temperature rises rapidly to 180 °C. The intensity of dehydration is lowered at the same time. After cooling, ready-to-use semi-aquatic (building) gypsum (*i.e.* gypsum hemihydrate) is obtained.

Peat bitumens

Physical and chemical properties

It is well known (Rakovskii *et al.* 1959, Lishtvan *et al.* 1983) that the organic substance of peat includes:

- substances that can be extracted by cold and hot water;

¹ The specific surface of β -calcium sulphate hemihydrate is 2–2.5 times that of α -calcium sulphate hemihydrate. Thus, although the α -hemihydrate sets more slowly than the β -hemihydrate when mixed with water, the α -hemihydrate has a higher hydration rate because its particles have a larger specific surface.

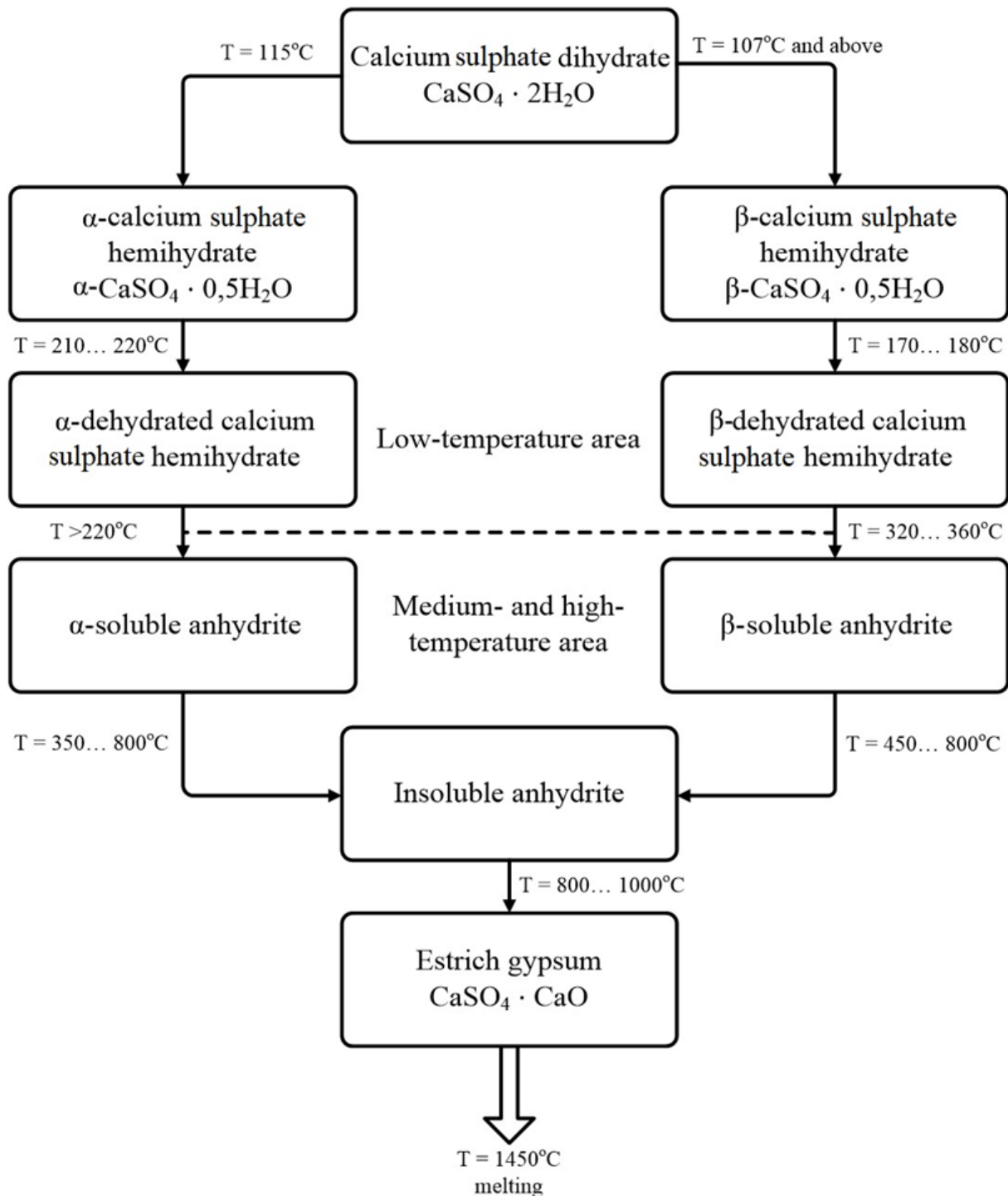


Figure 1. Scheme of formation conditions for the two modifications of calcium sulphate in their hydrated and anhydrous forms, according to Ferronskaya (2004). Low-temperature processes (up to $\sim 220^\circ\text{C}$) are described in the text. Upon further temperature increase (to 220°C and above for α -dehydrated hemihydrate, to $320\text{--}360^\circ\text{C}$ for β -dehydrated hemihydrate) there are changes in the crystal lattices and the hemihydrates convert into α -soluble and β -soluble anhydrites. The main differences in properties between soluble anhydrites and the precursor hemihydrates are higher water demand, quick setting and reduced strength (Ferronskaya 2004). Further thermal treatment in the range $360\text{--}800^\circ\text{C}$ results in complete rearrangement of the crystal lattices, converting the soluble anhydrites into insoluble anhydrite. The latter has very low solubility in water, and the solution hardly sets or hardens. In the next temperature range ($T = 800\text{--}1000^\circ\text{C}$) the insoluble anhydrite decomposes into calcium oxide, oxygen and sulphur dioxide. The product (Estrich-gypsum) obtained under these conditions is insoluble anhydrite with small amounts (2–3 %) of calcium oxide.

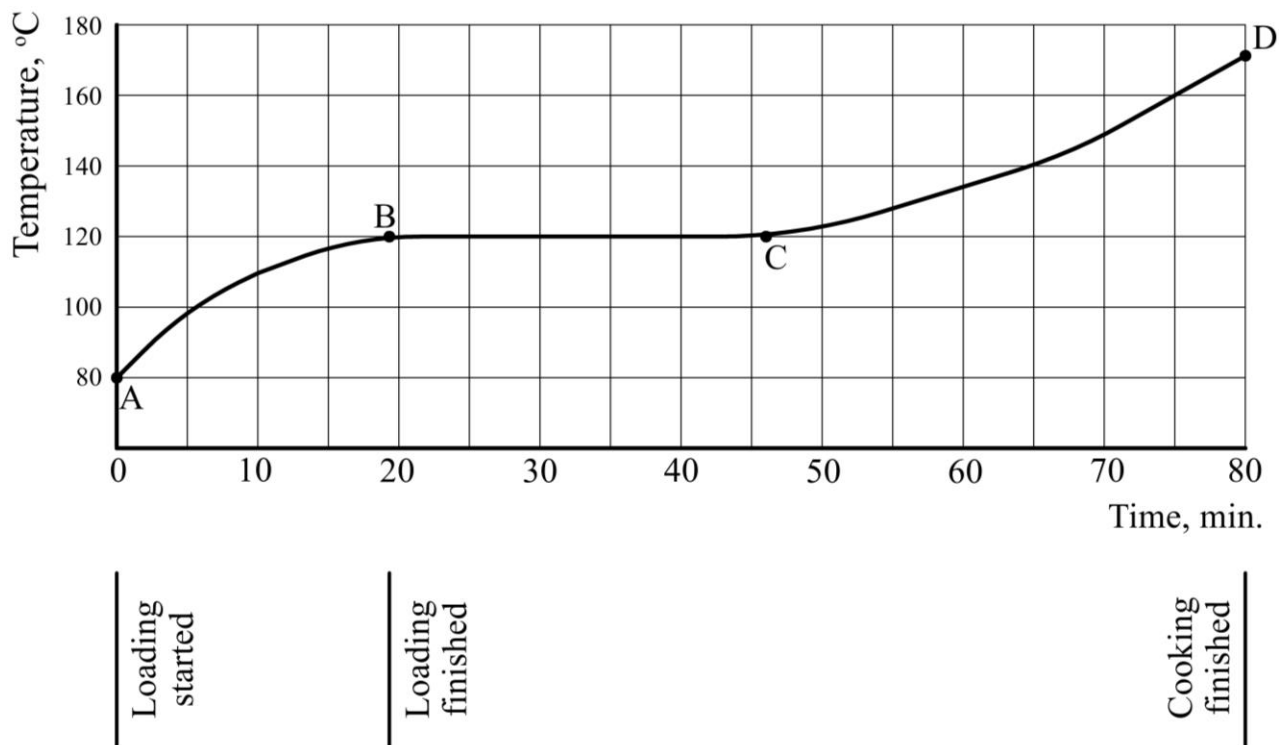


Figure 2. Temperature curve for the thermal treatment of gypsum binder.

- compounds that dissolve in water after hydrolysis in the presence of mineral acids (water-soluble and easily hydrolysed peat substances, cellulose);
- non-hydrolysable residue (lignin); and
- humic substances, which can be extracted from peat with a solution of alkali.

Products with different chemical composition and physical properties can be extracted using organic solvents (benzol, benzene, hexane, ether, dichloroethane, chloroform, *etc.*). Bitumens are amongst these (Bel'kevich *et al.* 1977, Bel'kevich *et al.* 1985). They represent the hydrophobic component of peat, and can be present both in a free state and bound to substances belonging to other groups. They also occur in, and can be extracted in the same way from, brown coals (Lishtvan *et al.* 2014).

According to modern understanding, bitumen is an oleophilic disperse system. The amorphous constituents of bitumens are oils and asphaltenes; and their crystalline components include paraffins, waxes and most of the individual constituents of waxes. The elementary structural unit, known as the micelle, consists of a condensed asphaltene core and a stabilising resin film. Resins impart viscosity and plasticity; their molecular weight decreases with distance from the asphaltene core and, at the extreme, approaches the range for oils. Oils act as the

dispersion medium. There is no clear differentiation between the dispersion medium and the micelle, which can be isolated only by removing oils and parts of resins using a selective solvent.

The description in the previous paragraph most closely represents petroleum bitumen, which has a highly developed coagulation structure and few crystalline constituents. In the bitumens of solid fuels, a crystalline structure (structural framework of cluster crystals consisting of waxes and paraffins) is more developed and imparts properties of rigidity, low elasticity and brittleness. The greatest quantities of crystalline substances (> 80 %) are found in brown coal bitumen extracted with benzol. Peat bitumen should be regarded as a crystalline structure that possesses plastic properties due to the high plasticity of its constituent crystals. At the same time, it may exhibit different structures, depending on the chemical composition of the peat and the extraction agent used.

While the macrostructure of bitumens varies between different solid fuels, their microstructure (the structure of the crystals) is the same for all bitumens and identical to that of the oil paraffin. The elementary crystalline cell of a bitumen is a rhombic face-centred lattice with parameters $a = 4.97 \pm 0.01 \text{ \AA}$, $b = 7.43 \pm 0.01 \text{ \AA}$, $c = 2.5 \pm 0.01 \text{ \AA}$ (Lishtvan *et al.* 1983). The higher the crystallinity of a bitumen, the more distinctive is the transition from

the solid to the free-flowing state². In structures with lower crystallinity, elastoplastic properties are strongly developed and the transition to viscous flow occurs slowly. In low-bitumen magellanicum peat there are small amounts of crystalline substance which do not form a solid crystalline structure, but grow together in individual needle-shaped crystals. On the other hand, high-bitumen pine-cottongrass peats contain considerable amounts (>60 %) of waxes, which form a typical crystal structure.

Bitumens are the most hydrogen-rich compounds in peat, containing waxes, oils, paraffins and resins (Table 1). Traditionally, the most valuable peat bitumens are those with high wax content. These waxes have relatively high melting points (in the approximate range 60–80 °C) and, even at low concentrations, dramatically increase the melting temperature and strength of various hydrocarbon alloys. They also have low electrical conductivity, relatively good strength (close to that of montan wax) and high resistance to moisture exposure. However, in the application proposed here, they form a glossy vitreous surface coating and it is necessary to pay attention to making sure that this coating does not increase the surface stickiness of the mineral binder.

Occurrence

The concentration of benzol bitumens in native peat varies within the range 1.2–17.7 % and depends on the nature of the peat. Among the peat-forming plants, dwarf shrub (heather) bushes contain the greatest amounts of bitumen, and mosses the smallest amounts (Naumova *et al.* 2015). Differences in the natural bituminousness of peat arise from differences in the initial bitumen content of the plants from which it is formed, as well as from secondary processes

Table 1. Composition of peat bitumens (%). From Smol'yaninov & Maslov (1975).

Bitumen components	Bog peat	Fen peat
waxes	16.63–55.66	42.39–80.94
resins	16.55–44.39	7.44–37.21
paraffins	4.40–11.40	2.41–5.99
oils	16.57–27.3	7.00–16.70

occurring within peat deposits (Lishtvan & Korol' 1975). The main characteristics that determine the bitumen content of peat are the degree of biochemical decomposition (bog peat) and the degree of saturation with inorganic compounds (fen peat).

Humic acids accumulate in peat as a result of decomposition. In bog peat, resinous components are synthesised during the condensation of humic acids with sugars and aldehydes, and humic acids are also converted to bituminous substances through their interactions with other products of incomplete decomposition (fibre, pectic substances, proteins, fats). In fen peat these processes are distorted by the influence of the mineral-water regime (Gamayunov & Gamayunov 2005). The bitumen content of fen peat is closely related to the composition of the ash, and is primarily associated with the calcium ion content and the acidity index (pH). Increasing the calcium content of peat reduces its bitumen content. A direct experiment on the same peat sample showed an increase in the yield of bitumens after removal of calcium (Bel'kevich *et al.* 1985; Table 2). Indeed, for

Table 2. Bitumen content values for fen peat with various contents of CaO in ash. Source: Bel'kevich *et al.* (1985).

Type of peat	R _t (%)	CaO content (%)	Bitumen content (%)	
			Initial peat	Decalcified peat
<i>Sphagnum</i>	15	0.76	6.14	8.0
sedge	20	1.45	5.92	6.1
	35	1.1	5.51	6.8
	45	3.84	2.49	3.3
<i>Scirpus</i>	45	1.22	7.14	8.3
wood	45	1.63	9.22	9.4
	50	1.15	8.86	10.0
	55	3.45	2.66	4.5

² This is especially important for justifying the pre-set hydrophobic regime of gypsum.

fen and transitional peat types, a reliable prediction of bitumen content can be obtained by considering the cation composition and the acidity of the peat.

Peat types can be arranged in order of increasing average bitumen content as follows: fen peat < transitional mire peat < bog peat. Fen peat varies little in its bitumen content. However, amongst all peat types there is a general trend of increasing bituminousness with degree of biochemical decay R_t . The degree of biochemical decay is the percentage of decomposed plant mass (humus) and the smallest fragments of its tissues which have lost their cellular structure (Lishtvan & Korol' 1975)³. The relationship between bituminousness and R_t is most apparent for bog peat (Naumova *et al.* 2013), and it is very weak for fen and transitional peat. The bitumen content of bog peat increases as the content of wood relative to moss species increases. Thus, ordering bog peat types in terms of bituminousness (benzol bitumens) reveals the following descending sequence: pine-cottongrass > cottongrass > pine-sphagnum > pine > scheuchzeria > cottongrass-sphagnum > scheuchzeria-sphagnum > magellanicum > sphagnum-ridge > fuscum (Lishtvan & Korol' 1975).

Purpose of this study

The general aim of this research is to develop a method for manufacturing hydrophobised gypsum binders by applying nano-films of peat bitumen to the surfaces of the gypsum particles during the industrial calcination of gypsum dihydrate. When hydrophobically modifying gypsum binders using the method of Misnikov (2016), sufficient peat must be introduced into the raw mix to ensure that continuous bitumen film coatings are formed on the mineral particles. On the other hand, an excessive amount of organic ballast can predispose the gypsum to reduced strength when hardened. Therefore, in selecting the organic raw material, preference should be given to peat with bitumen content > 4%. However, it may be possible to obtain satisfactory results using less-bituminous peat at a theoretical concentration determined using the method developed by Misnikov (2006, 2016) with further empirical optimisation. The ash content of the peat must also be considered, especially for fen peat with high degree of decomposition ($R_t > 30\%$) and any type of peat with artificially increased ash content. The study described here involved laboratory testing of two contrasting peat types as hydrophobisation agents, taking these factors into consideration.

METHODS

The mineral raw material used in the experiments was gypsum from the Shushokskoye deposit (Republic of Adygea, Russia), whose calcium sulphate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) content is > 93% (supplier's information). The gypsum rock was milled in a ball mill until the powder reached a specific surface of 320–350 $\text{m}^2 \text{kg}^{-1}$, determined using a standard ПСХ-12 SP gas permeability meter (Kozeny-Carman method).

For hydrophobisation of the gypsum, two samples of peat (both collected in Russia) were prepared. Their characteristics are presented in Table 3. The bog peat was collected from the "Kurovskoye" peat deposit in Tver region, and the fen peat came from the "Mokeiha-Zybinskoe" peat deposit in Yaroslavl region. These peats were chosen on the basis of bitumen content, which was adequate (4.7%) in the bog peat and below the recommended level (2.1%) in the fen peat. The peat was dried to constant weight in a drying oven at 105 °C then ground to achieve particle sizes comparable to those of the gypsum and sieved (mesh size 100 μm). It was then added to the gypsum dihydrate at different specified concentrations (recalculated to take account of its ash content *per* unit amount of organic matter) that ranged from 0.5% to 5%. The mixture was thoroughly blended in a paddle mixer and placed in an automatic drying oven. The heat treatment (aerobic regime) applied to the experimental samples in the drying oven corresponded to the temperature and time schedule presented in Figure 2. Treatment of the control sample - gypsum dihydrate powder without a peat additive - was carried out under the same conditions.

The samples were then cooled to room temperature and prepared for further experiments to assess their degree of hydrophobicity. As a preliminary qualitative assessment, water was poured onto the surface of each sample. If the water was not absorbed (Figure 3), this was taken to confirm that hydrophobisation had occurred, and the water repellent properties of the sample were subsequently quantified.

Quantitative assessment of hydrophobic properties was based on two indicators, namely the water-repellency of the powder and its ability to absorb water vapour. The method for determining water-repellency was based on a visual assessment of the time for which a drop of water remained on

³ Comparisons of the peat decomposition scales used in western countries (The Von Post and Valgren Scale of Peat Decomposition) with the scale used in the CIS (Commonwealth of Independent States) countries are given by Bazin *et al.* (1992) and Malterer *et al.* (1992).

Table 3. Characteristics of the peat raw materials used.

Characteristics of materials	Peat type	
	cottongrass-sphagnum bog peat	woody-sedge fen peat
degree of decomposition (R_t) (%)	45	55
ash content (A^c) (%)	5.8	15.4
acidity (pH) of salt extract	3.9	5.3
group chemical composition of organic part (%):		
bitumens	4.7	2.1
humic acids	37.5	48.9
fulvic acids	23.6	20.6
water-soluble and readily hydrolysable	19.9	17.4
hardly hydrolysable	11.9	9.8
cellulose	2.4	1.2



Figure 3. Options for preliminary tests of the hydrophobicity of modified gypsum binder.

the surface of a layer of the powder. About 50 g of powder was placed in a Petri dish and its surface was levelled by gently shaking the dish. Then, at least ten drops ($\sim 0.1 \text{ cm}^3$ per drop) of distilled water were placed on the surface, at least 10 mm apart, using a pipette held with its tip at a height of 0.5–1 cm (Figure 4). A stopwatch was used to measure the (retention) time during which each of the droplets remained on the surface of the powder, prior to soaking in. This experiment was replicated three times for each treatment and the arithmetic mean

value of moistening time for at least 30 individual drops was calculated.

The water vapour absorption of gypsum was determined on samples that had been previously dried to constant weight at a temperature of 45–55 °C. About 50 g of the powder samples (three replicates in each case) were put into Petri dishes and placed in a laboratory desiccator containing a small amount of distilled water so that they did not touch the surface of the water. The desiccator was then closed with an airtight cover. In such conditions, the



Figure 4. Petri dish containing modified gypsum powder, with drops of water applied to the surface.

relative humidity of the air above the water surface is 100 %. The mass increments of the samples were determined daily for seven days, by weighing to two decimal places on a laboratory balance. At the end of the experiment, the samples were again dried at 45–55 °C and weighed.

To assess the effect of the organic component on the strength of the hardened gypsum solution, the following method was used to determine the maximum destructive load. Moulded samples of gypsum binder were produced by mixing two parts (by weight) of gypsum binder powder with one part of tap water. The gypsum binder was poured into a dish containing the water within 5–20 seconds, with constant mixing. After this, vigorous stirring was continued in an automatic mixer for 60 seconds until a homogeneous paste was obtained. The paste was poured into cylindrical plastic moulds (diameter

30 mm, height 50 mm) which were vibrated (amplitude 1 mm, frequency 50 Hz) for five seconds to remove entrained air. The samples were allowed to harden for two hours, then they were removed from the moulds and subjected to destruction under uniaxial compression. The strength of the sample σ (MPa) is the maximum destructive load (force) F_{\max} (N) per unit cross-sectional area of the sample. The strength limit (breaking point) of each type of material was calculated as the arithmetic mean of the results for five samples, excluding the largest and smallest values obtained. Because all the samples had the same cross-sectional area and height, in this study it was practical to evaluate relative strength σ_{rel} as:

$$\sigma_{\text{rel}} = \sigma_{\text{max}} / \sigma_i \quad [3]$$

where σ_{max} is the strength of the control sample (no additives) and σ_i is the strength of the experimental sample (with additive). Thus, for the control sample, $\sigma_{\text{rel}} = 1$.

RESULTS

Table 4 shows the retention times for water droplets placed on the surface of the gypsum binder with different concentrations of bog and fen peat additive. The hydrophobisation effect occurred even at the lowest concentration of peat additive tested (0.5 %), with the droplet retention time increasing from 0.03 minutes in the control to 11.48 minutes in the binder modified with fen peat and to 17.35 minutes in the binder modified with bog peat. In all cases, the water-repellency of the powder increased with the concentration of additive. The maximum retention observed was 31.09 minutes for binder treated with 1.5 % of bog peat. It is expected that the water-

Table 4. Retention times (decimal minutes) of water droplets on the surface of gypsum binder. The values are arithmetic means of the absorption times for 30 drops. Standard deviation (squared) is not shown for the control sample because absorption occurred so rapidly that it was almost impossible to time.

Factors	Control sample	Experimental samples with peat additive					
		bog peat			fen peat		
Concentration of additive (%)	0	0.5	1	1.5	0.5	1	1.5
Moistening time (min)	0.03	17.35	21.30	31.09	11.48	16.47	24.73
Mean standard deviation (squared)		2.69	3.17	4.38	1.73	2.42	3.44

repellency of the binder would increase with further increases in additive concentration (Misnikov 2006), but this would not be useful due to the accompanying drop in strength (see later).

The progress of water absorption during the experimental simulation of storage at 100 % relative humidity, carried out in the desiccator, is shown in Figure 5. The gypsum binder that was hydrophobically modified using bog peat at concentrations of 0.5–1 % absorbed around half the amount of water absorbed by the unmodified control material. However, doubling the additive concentration (from 0.5 % to 1 %) did not result in a

proportional decrease in water vapour absorption. This provides additional evidence for the formation of continuous bitumen films on the mineral particles.

Figure 6 shows the dependence of relative strength (σ_{rel}) of the moulded gypsum binder on the concentration of peat additive. The curve obtained can be divided into three sections, which characterise the hardening process. At additive concentrations of 0–1.5 % there was no critical decrease in the strength characteristic. Strength declined steeply as the concentration of the organic component increased from 1.5 % to 3.5 %, then tended to stabilise again at concentrations of 3.5–5 %.

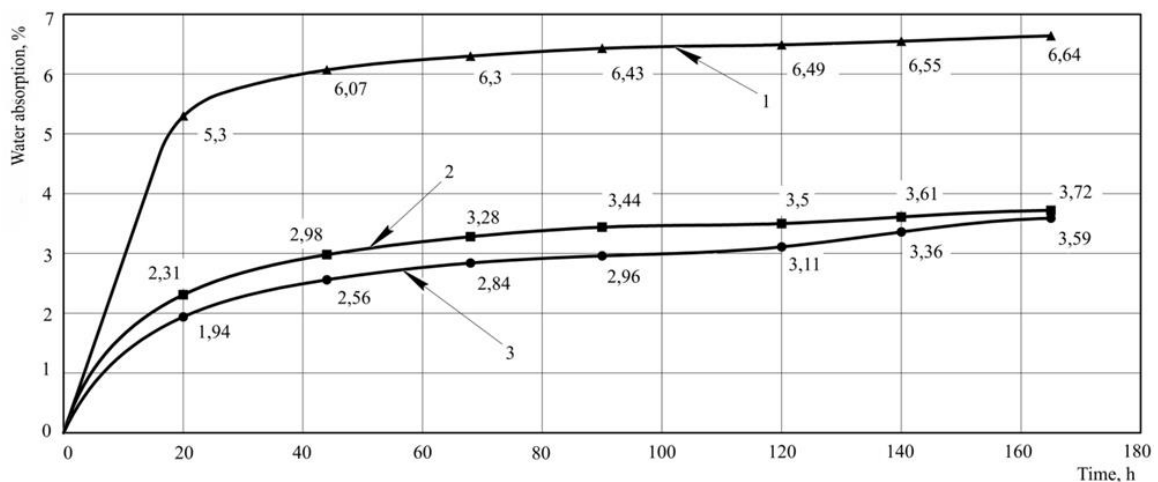


Figure 5. Decrease in speed and capacity of water vapour sorption during storage of gypsum binder under 100 % relative humidity; 1: control sample; 2: with 0.5 % additive (bog peat); 3 with 1 % additive (bog peat).

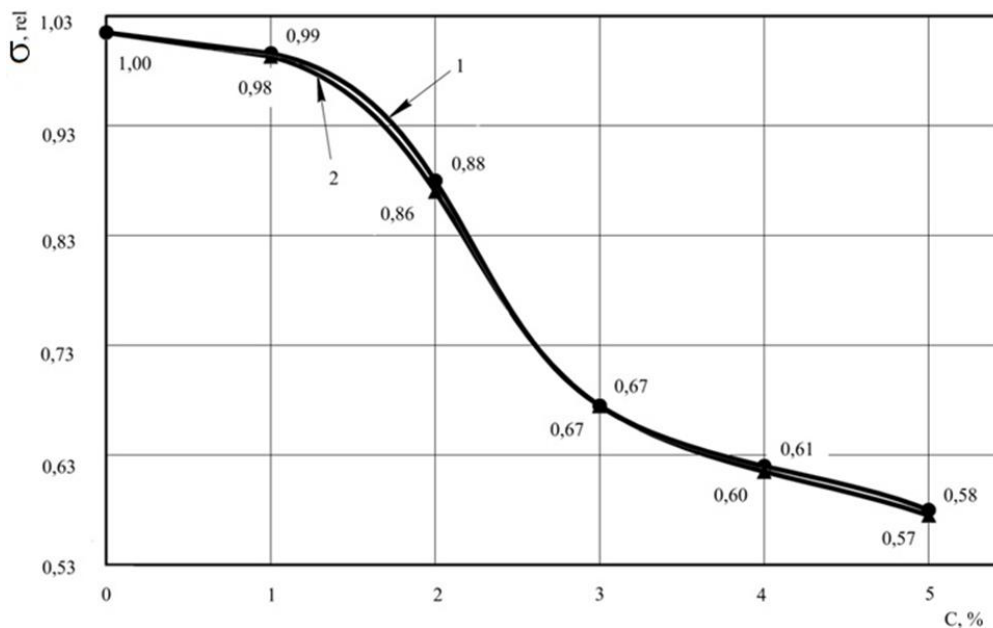


Figure 6. Dependence of the relative strengths (σ_{rel}) of experimental samples of gypsum binder on the concentration (C) of peat-based organic additive (1: bog peat; 2: fen peat).

DISCUSSION

Performance of the peat additives

When heat treatment is applied to the control sample, crystalhydrate moisture separates in accordance with one of the reaction mechanisms shown in Equations 1 and 2. In the experimental samples, hydrophobisation of the mineral particles of the gypsum binder by peat bitumens is assumed to occur concurrently with moisture separation, according to the mechanism established by Misnikov (2016). Moreover, during the thermal process of hydrophobic modification, humic acids are destroyed (Bazhenov *et al* 1999) and resinous nitrogen- and oxygen-containing substances are formed (Rakovskii *et al* 1959). This allows additional bitumen components to be obtained, especially when using fen peat. These will form a film coating on the gypsum particles alongside native bitumens from the peat.

The experiment to investigate the water-repellency of treated gypsum binder showed (Table 4) that an effect occurred even at the lowest concentration of peat additive that was tested (0.5 %), and this was the case for both bog peat and fen peat. However, when choosing raw materials, preference should still be given to bog peat because it has higher bitumen content and lower ash content than fen peat. Using the calculation method developed for treatment of cement, Misnikov (2016) found that continuous bituminous film coatings were formed on the surfaces of the mineral particles when the concentration of peat additive was only 0.5 %. During heat processing the gypsum particles may retain, *per* unit area, only the amount of bitumen which is determined by the energy of its interaction with the mineral surface. The minimum thickness of a continuous film of peat bitumens that can be formed on the surfaces of modified gypsum particles will probably be in the same range (11–22 nm) as was previously determined for cement (Misnikov 2016). The further increase in water-repellency that was observed at higher peat concentrations was expected, since the increased amount of organic hydrophobic particles (from modified peat) in the gypsum would increase the thickness of the protective films. However, in order to maintain the strength of gypsum products, it is necessary to keep the concentration of organic additive as low as possible.

Water repellency is only one indicator of the degree of hydrophobicity of the material. Surface repulsion of liquid does not confirm the presence of a continuous film coating because it can also occur in porous structures that have ‘islands’ of hydrophobic inclusions. However, structures of the latter type will be completely permeable to water vapour. Any water

vapour that enters the structure will subsequently condense to form liquid moisture whose presence within the powder will, with time, lead to premature hydration of the mineral binder. A more reliable indicator of hydrophobicity is the vapour absorption of gypsum stored in air with relative humidity $\varphi = 100\%$. When such storage conditions were simulated experimentally, the results confirmed that a substantial reduction in water absorption occurred in the treated samples. This is consistent with the presence of a protective barrier against water molecules on the particles after heat treatment in the presence of peat. With the initial bitumen content of the bog peat used (4.7 %), the additive concentration of 0.5 % is already sufficient to form a continuous coating. As can be seen from Figure 5, increasing the additive concentration to 1 % does not give any significant qualitative improvements. It is not useful to carry out experiments on gypsum binder with higher concentrations of peat additive because the organic matter in the peat promotes the growth of defects in the structure of the binder after hardening. The optimal concentration may be higher for other mineral materials; for example, it was 2.0 % for cement (Misnikov 2016). If using fen peat with the characteristics given in Table 3, it would be necessary to at least double the concentration of additive on account of its low bitumen content (2.1 %) and its high ash content (15.4 %). At these concentrations, the additive would adversely affect the strength of the binder (Figure 6).

The process of water vapour absorption by gypsum binders is divided into three stages - two basic (initial and final) and a transition (intermediate). The durations of these stages depend on the degree of hydrophobicity of the powder. For example, for a control sample, the initial stage lasts 0–20 hours, the intermediate stage has a duration of 20–40 hours, and the final stage lasts from 40 hours to the end of the experiment (in this case, seven days or 168 hours). In modified samples, the durations of the stages are approximately 0–5, 5–20 and 20+ hours. Although the kinetics of vapour absorption by the various powders (Figure 5) may seem qualitatively similar, the physical and chemical processes occurring during their successive stages are different. In the control sample (top curve (1) in Figure 5), the initial stage involves water vapour penetrating into the pore spaces between the gypsum particles, if possible filling them to capacity. Then, during the transitional stage, the water vapour condenses into liquid moisture which starts to interact with the mineral powder and, as a result of the hydration, the gypsum sets. This process differs from homogenous mixing with water (the standard

method for obtaining a gypsum solution) in that it is stochastic and results in the formation of small lumps of partially hydrated gypsum of varying size (1–5+ mm). At the final stage, the mass increment occurs due to incorporation of the moisture into the gypsum material. The ability of the gypsum binder to provide quality gypsum solutions is then lost until the mechanical and thermal treatment at 140–180 °C (see Introduction) is repeated. In the experimental samples (lower curves (2, 3) in Figure 5) the same mechanism is partially reproduced, but it is not determinative. Here, when water vapour penetrates into the pore space during the initial stage, it remains there due to the presence of the protective film on the particles. When condensation occurs, liquid moisture also accumulates in the pore space and is partly absorbed by the organic particles of the peat additive. However, this process is reversible, as the moisture can be removed at relatively low drying temperatures (up to 105 °C). It is also important to note the extreme conditions (relative humidity $\phi = 100\%$) of the experiment. Under normal storage conditions ($\phi \ll 100\%$), the hydrophobically-modified gypsum binder would be immune to the negative effects of water vapour even if it were not contained in polyethylene packaging.

The results for the progress of water vapour absorption are qualitatively similar to those previously obtained for Portland cement powder by Misnikov (2016). However, the water-repellency of gypsum binder is quantitatively lower than that of cement. To explain these results, it will be necessary to conduct additional experiments that take into account the differences between cement and gypsum in terms of the specific surface areas of their particles, the temperature and humidity conditions during processing, and their component compositions. Cement is a complex multicomponent system containing clinker, calcium sulphate dihydrate and various types of modifying additives. In contrast, gypsum powder is a one-component system, which significantly simplifies forecasting of the physical and chemical processes taking place within it, during both acquisition and use. The hydrophobic modification of these materials by peat additives will lead to additional complexities in the mechanisms under study. Considering the hydrophobic processing itself, the processes occurring in cement are simpler. This is because there is practically no disengagement of water during the thermal exposure of cement in the relevant temperature range, whereas for gypsum the probability of a negative effect associated with simultaneous removal of water and bituminous components from the reaction zone is higher. Nevertheless, the experiments reported here yielded

reliably reproducible data, indicating an improvement in the quality characteristics of the modified gypsum binder.

It is important to ensure that applying a water-repellent treatment to gypsum binders does not affect the strength of the final gypsum products. The action of various types of hydrophobic additives will tend to reduce strength for two main reasons. First, such additives will hinder the hydration process when gypsum solutions are required. Secondly, organic particles (introduced as carriers of bitumen) will remain in the gypsum after setting, and increase the number of defects in its structure. This problem is solved by quantitative (as a rule, empirical) optimisation of the additive concentration. Dependence analysis of the relationship $\sigma_{rel} = f(C)$ for gypsum binder (Figure 6) showed that there was no critical decrease in the strength characteristic when the concentration of the hydrophobising peat additive was 0.5–1 %. There was also no increase in the activity or setting time of gypsum samples. But at the same time, the shelf life increased significantly, even under adverse conditions. When the concentration of the organic component was greater than 1.5–2 % there was a decrease in the strength of the gypsum, as expected on the basis of the reduced number of contact interactions in the gypsum caused by defects in its structure due to the presence of the organic component. Portland cement that has been modified using fen peat as a hydrophobising additive shows a significant decrease in strength only when the peat concentration exceeds 2 % of the mass of mineral binder. With 1 % of an additive based on bog peat with degree of decomposition $R_t = 25\%$, a slight increase in flexing and compression strength is observed (Misnikov 2016). Moreover, the characteristics of the relationships between strength and additive concentration obtained for gypsum binder (Figure 6) differ strongly from those of the equivalent relationships for cement. For gypsum binder, the curves are clearly divided into the three sections described above (Results section), whereas those for cement take the form of relatively smooth curves (Figure 8 in Misnikov 2016).

Prospects for industrial implementation of the method

The method has great prospects for uptake by the industry, since it is practical to implement it in existing industrial production systems. A structural scheme for realisation of the method is shown in Figure 7. This assumes implementation by either joint grinding of gypsum stone and a semi-finished peat additive, or mixing of gypsum powder with the additive. In both cases, the peat may be obtained

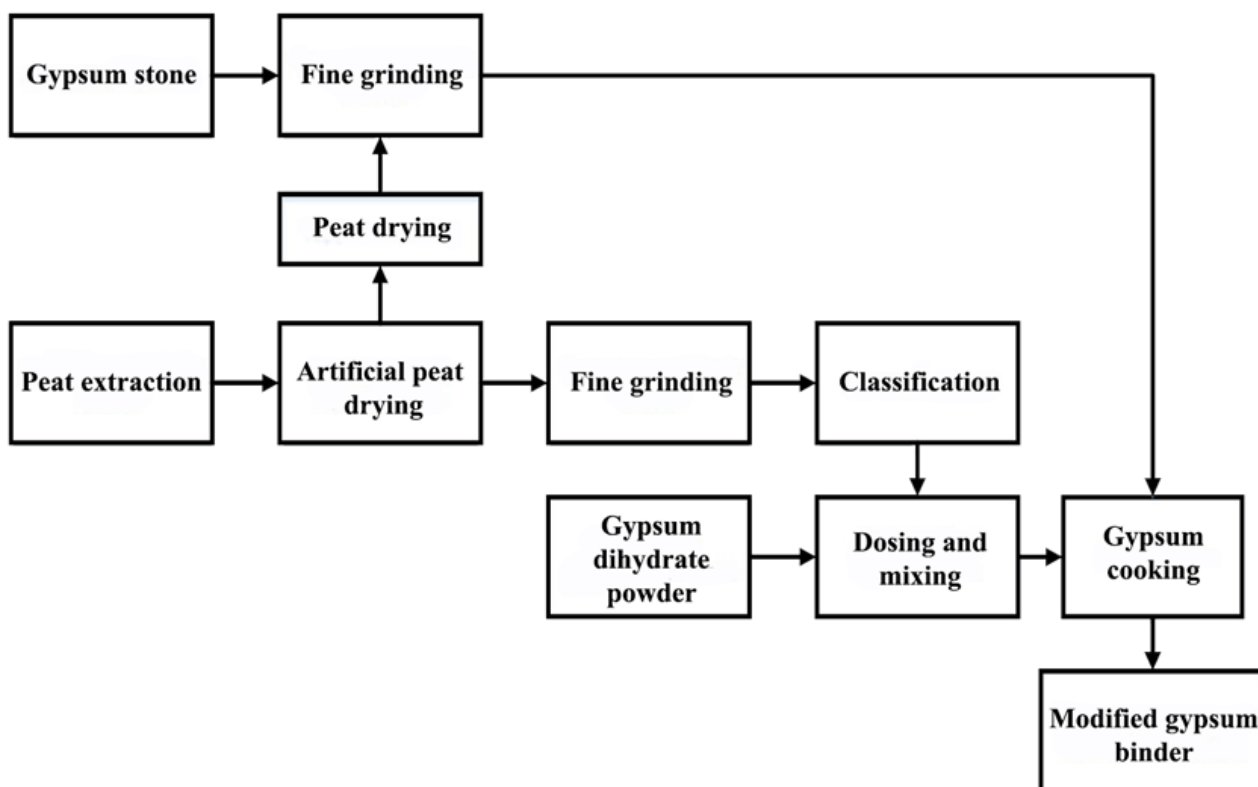


Figure 7. Structural scheme for the production of modified gypsum binder.

using any of the traditional technologies (*e.g.* milled or sod peat). However, preference should be given to technology that produces peat with the lowest possible moisture content (Efimova & Pukhova 2013). As a rule, this is milled peat, which can be extracted pneumatically. The raw material can also be sod peat obtained using machines that combine the operations of excavation and moulding. The use of these technologies makes it possible to produce peat with a moisture content of 35–40 %, and the peat is subsequently subjected to artificial drying to achieve a moisture content of 10–16 %.

Dried peat at the required concentration may be added to the mill which grinds the gypsum stone, and the two raw materials milled together. The resulting mixture is put into a cooking boiler where the gypsum is heated under the conditions shown in Figure 2. The other option is that the dried peat is subjected to fine milling and sorting with separation of the fraction with particle size < 100 μm . The resulting organic powder is then mixed with gypsum powder before firing. It is expected that the cost of finished gypsum binder prepared by this method would be higher than for the previous option (co-milling). However, it is still a promising prospect for industrial use because it allows diversification of products in non-core factories.

As an example, we can use a standard technological scheme for the production of gypsum binder using batch cooking boilers (Figure 8). Analysis of the process equipment confirms that it is possible to install an additional bunker with a feeder for artificially dried milled peat. From this bunker, peat will flow into the bin feeder and through the disk feeder along with the crushed gypsum stone, and thence to the shaft mill. The size of the gypsum stone pieces used in this scheme is 300–500 mm, and they undergo primary crushing in jaw crushers which reduces them to 30–50 mm. If necessary, secondary crushing can be carried out in hammer crushers to achieve a particle size of 0–15 mm. Fine grinding of the crushed stone is carried out in a shaft mill (hammer mill with gravity separator) which may also be capable of drying the gypsum and, in some cases, firing the raw-ground gypsum powder (for example, when manufacturing medical gypsum). Inclusion of this element would make it possible to use a cheaper semi-finished peat product that had not been subjected to artificial drying, thus tending to further reduce the production cost of hydrophobically modified gypsum binder.

The temperature of the gases at the entrance to the mill is in the range 300–500 °C. The movement of gases in the system is forced by the operation of

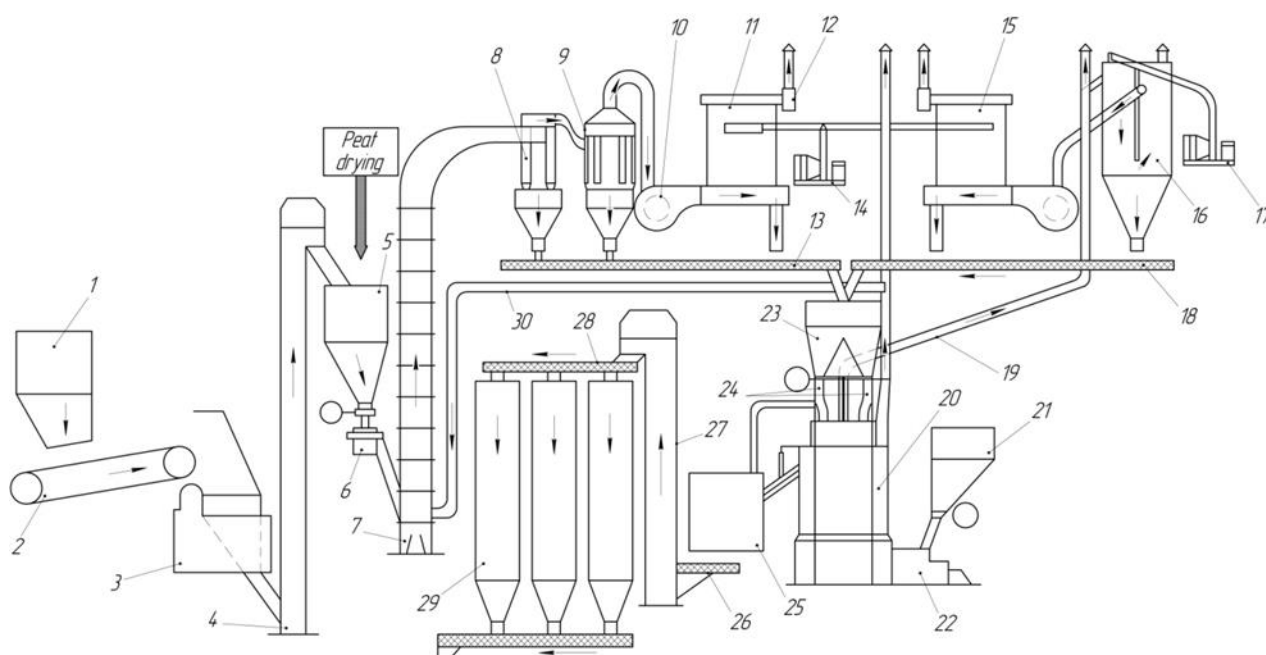


Figure 8. Technological scheme for the production of modified gypsum binder. 1: gypsum stone bunker; 2: conveyor belt; 3: jaw crusher; 4: chain elevator; 5: bin feeder for crushed gypsum rock; 6: disk feeder; 7: shaft mill (paddle type); 8: cyclones; 9: cyclones battery; 10,12: fans; 11,15: sleeve filters; 13,18: screw conveyors; 14,17: heaters; 16: dust condensing chamber; 19: steam pipe; 20: gypsum cooker; 21: solid fuel bunker; 22: furnace; 23: gypsum powder bunker; 24,26: feeders; 25: malleable bunker; 27: elevator; 28: screw conveyor; 29: gypsum binder silo; 30: gas pipe.

centrifugal fans. The fineness of the powder produced by joint grinding of the raw materials, as well as throughput, is regulated by the speed of gas flow. After leaving the mill, the gas-and-dust mixture passes through dust-collecting devices (cyclones, cyclone batteries, sleeve filters and electrical filters). The mixture of gypsum powder and peat additive precipitated in the dust-cleaning system will then flow into the supply bunker, which is located above the cooker. Depending on the temperature of the flue gases when exiting from the mill (85–105 °C), the temperature of the powder can vary from 70 to 100 °C. This will be sufficient to reduce (if necessary) and equalise the moisture content of the mixture. The gypsum is cooked in gypsum cookers with constant stirring. The duration of cooking and temperature ranges should correspond to the temperature curve shown in Figure 2.

Thus, the results of this study will enable us to develop an industrial technology for the production of gypsum binder with hydrophobic modification by peat additives. Because the proposed method is completely adapted to the processes currently used in the production of gypsum, it does not require any technological equipment changes. Optimisation of the quantitative composition of peat additives will allow us to obtain hydrophobically-modified gypsum

binder with low sorption capacity for water vapour without changing its strength grading. Moreover, the proposed implementation would not lead to an increase in cost of the modified product, as the price of the semi-finished peat additive is similar to the cost of raw gypsum.

REFERENCES

- Bazin, E., Kopenkin, V., Kosov, V., Korchunov, S. & Petrovitch, V. (1992) *Tekhnicheskiy analiz torfa (Technical Analysis of Peat)*. Izdatelstvo «Nedra» (Nedra Publishing House), Moscow, 431 pp. (in Russian).
- Bazhenov, D., Tarnovskaya, L. & Maslov, S. (1999) *Fiziko-khimicheskie osnovy modelirovaniya reaktsiy termoliza torfa. Guminovyye i fulvokisloty (Physical and chemical bases of modelling of peat hydrolysis reactions. Humic and fulvic acids)*. *Khimiya Rastitelnogo Syriya (Chemistry of Plant Raw Materials)*, 4, 39–46 (in Russian).
- Bel'kevich, P., Gaiduk, K., Zuev, T. & Ivanova, L. (1977) *Torfyanoi Vosk i Soputstvuyushchie Produkty (Peat Wax and By-products)*. Izdatelstvo «Nauka i Tekhnika» (Science and Technology

- Publishing House), Minsk, 232 pp. (in Russian).
- Bel'kevich, P., Golovanov, N. & Dolidovitch, E. (1985) *Khimiya Ekstraktsionnykh Smol Torfa i Burogo Uglya (Chemistry of Peat and Brown Coal Extraction Tars)*. Izdatelstvo «Nauka i Tekhnika» (Science and Technology Publishing House), Minsk, 168 pp. (in Russian).
- Efimova, E. & Pukhova, O. (2013) Izmenenie vodno-fizicheskikh svoystv torfyanogo syr'ya pri mehanicheskoy pererabotke i sushke. (Changes in the water-physical properties of peat raw material upon mechanical processing and drying). *Trudy Instorfa (Proceedings of Instorf)*, 8(61), 44–47 (in Russian).
- Ferronskaya, A. (2004) *Gipsovyie Materialy i Izdeliya (Proizvodstvo i Primenenie) (Gypsum Materials and Products (Production and Use))*. Izdatelstvo Assotsiatsii Stroitel'nykh Vuzov (The Association of Building Universities), Moscow, 488 pp. (in Russian).
- Gamayunov, N. & Gamayunov, S. (2005) Mass transfer in peat. *Eurasian Soil Science*, 38(3), 297–304.
- Gorchakov, G. & Bazhenov, Y. (2012) *Stroitel'nye Materialy (Construction Materials)*. Kniga po trebovaniyu (Book on Demand), Moscow, 688 pp. (in Russian).
- Khigerovich, M. & Baier, V. (1979) *Gidrofobno-Plastifitsiruyushchie Dobavki Dlya Tsementov, Rastvorov i Betonov (Hydrophobically-Plasticising Additives for Cements, Mortars and Concretes)*. Stroyizdat, Moscow, 125 pp. (in Russian).
- Lishtvan, I. & Korol', N. (1975) *Osnovnye Svoistva Torfa i Metody ikh Opredeleniya (Basic Properties of Peat and Methods for their Determination)*. Izdatelstvo «Nauka i Tekhnika» (Science and Technology Publishing House), Minsk, 319 pp. (in Russian).
- Lishtvan, I., Terent'ev, A., Bazin, E. & Golovach, A. (1983) *Fiziko-khimicheskie Osnovy Tekhnologii Torfyanogo Proizvodstva (Physical and Chemical Basis of Peat Production Technologies)*. Izdatelstvo «Nauka i Tekhnika» (Science and Technology Publishing House), Minsk, 232 pp. (in Russian).
- Lishtvan, I., Dudarchik, V., Kraiko, V., Bulgakova, N., Anufrieva, E. & Smolyachkova, E. (2014) Pyrolysis of mixtures based on the oil shale and brown coal of Belarus and the characterization of the resulting fuel products. *Solid Fuel Chemistry*, 48(2), 75–80.
- Malterer, T., Verry, E. & Erjavec, J. (1992) Fiber content and degree of decomposition in peats: review of national methods. *Soil Science Society of America Journal*, 56(4), 1200–1211.
- Misnikov, O. (2006) Physicochemical principles of hydrophobization of mineral binders by additives produced from peat raw material. *Theoretical Foundations of Chemical Engineering*, 40(4), 423–430.
- Misnikov, O. (2014) A study of the properties of portland cement modified using peat-based hydrophobic admixtures. *Polymer Science Series D*, 7(3), 252–259.
- Misnikov, O. (2016) Scientific basis of a new method for hydrophobic modification of mineral binders using peat products. *Mires and Peat*, 18(22), 1–15.
- Misnikov, O. & Chertkova, E. (2014) Hydrophobic modification of mineral binders by additives produced from peat. *Eurasian Mining*, 1(21), 63–68.
- Naumova, G., Tomson, A., Zhmakova, N., Makarova, N. & Ovchinnikova, T. (2013) Phenolic compounds of *Sphagnum* peat. *Solid Fuel Chemistry*, 47(1), 22–26.
- Naumova, G., Tomson, A., Zhmakova, N., Makarova, N. & Ovchinnikova, T. (2015) Biologically active compounds of different sphagnum peat species. *Solid Fuel Chemistry*, 49(3), 135–140.
- Rakovskii, V., Kaganovich, F. & Novichkova, E. (1959) *Khimiya Pirogennykh Protsessov (Chemistry of Pyrogenic Processes)*. Izdatelstvo AN BSSR (AN BSSR Publishing House), Minsk, 208 pp. (in Russian).
- Smol'yaninov, S. & Maslov, S. (1975) *Termobriketirovanie Torfa (Hot Briquetting of Peat)*. Izdatelstvo Tomskogo gosudartstvennogo universiteta (Publishing House of Tomsk State University), Tomsk, 108 pp. (in Russian).
- Sulman, M., Kosivtsov, Yu., Sulman, E., Alfyorov, V., Lugovoy, Yu., Molchanov, V., Tyamina, I., Misnikov, O., Afanasjev, A., Kumar N. & Murzin, D. (2009) Influence of aluminosilicate materials on the peat low-temperature pyrolysis and gas formation. *Chemical Engineering Journal*, 154, 355–360.

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