

# Use of Deep Peat-Processing Products for Hydrophobic Modification of Gypsum Binder

Oleg Misnikov<sup>1\*</sup>, Valeriy Ivanov<sup>1</sup>

<sup>1</sup>Tver State Technical University, A. Nikitin Street, 22, 170026, Tver, Russia

**Abstract.** The article deals with the issue of gypsum binder quality reduction during its storage and transportation. The study provides the main methods to protect gypsum from unauthorized exposure to moisture and water vapor. The author proposes hydrophobic modification as a perspective method for the preservation of gypsum activity and its water absorption reduction. The substantiation of cement hydrophobization with the bitumen released during peat thermolysis is provided. The author proposes to use this method in the technology of gypsum binder production. The basic idea is to combine the hydrophobization process with the calcination of calcium sulfate dehydrate. This is facilitated by temperature ranges used for dehydration of natural gypsum and the initial stage of thermal decomposition of the organic matter of peat. The author defined experimentally an optimal concentration of the organic component in gypsum binder. After adding 0.5-1% of the peat additive, the gypsum plaster preserved its grade strength and increased its storage time without caking and hydration, also under adverse conditions. The proposed method is adapted to the technological processes presently used in the production and doesn't require changing any equipment. The price of mineral raw materials and semi-finished products of peat are approximately equal which reduces the probability of increasing of the cost of hydrophobically modified gypsum binder.

## 1 Introduction

Gypsum binder (gypsum hemihydrate), used in the construction industry, is a fine powder obtained from natural gypsum dihydrate by heat treatment in the temperature range 140-190°C. Gypsum dihydrate refers to quick-setting and quick-hardening miner binding materials. It is widely used for plastering, manufacturing of gypsum concrete, gypsum building products, castings, forms, and as an additive to other binding materials [1].

One of the main issues of using gypsum binder is its activity reduction over time. This is due to its hygroscopicity. The intensity of the absorption of water from the atmosphere depends on the humidity and ambient temperature. This leads to a gradual transformation of gypsum hemihydrate into the dihydrate one during storage, and reduces its activity upon

---

\* Corresponding author: [oleg.misnikov@gmail.com](mailto:oleg.misnikov@gmail.com)

setting and hardening. The longest storage life is considered to be three months – during this period the activity of gypsum binder reduces on average by 30-50%. Moreover, the high water absorption of gypsum-based building materials results in low frost resistance. It does not allow them to be used for exterior works without additional treatment by traditional hydrophobic compounds [2, 3].

By now we know a number of methods for increasing water repellent properties of mineral dispersed materials [4]. According to their effect they can be divided into two main groups. The first group includes the additives that have inherent hydrophobic characteristics. They are obtained from animal and plant raw materials, as well as from some minerals and are called “hydrophobic additives”. The second group, called “hydrophobizing additives”, includes materials and chemical compounds that do not possess inherent hydrophobic properties but acquire them during their interaction with mineral binders.

There are several established methods for the protection from exposure to moisture and water vapor. For example, hygroscopic materials can be stored in dry places in an airtight plastic container. Another method is the processing of their particles with isolating coatings or their powdering with flowing agents. The use of this method prevents or hinders the access of water molecules to the protected particles. In this case an isolating protective film, liquid or solid flowing agent should possess a high water-repellant property – hydrophobicity.

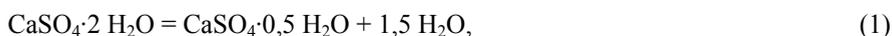
Peat is one of the natural organic materials, which can be used as a raw material for obtaining hydrophobic coatings. Its known reserves in the Russian Federation are about 186 billion tons (37% of global reserves).

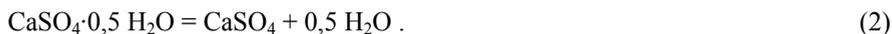
During drying, peat passes from hydrophilic to partially hydrophobic state, during which its water-absorption capacity reduces considerably. The natural hydrophobicity of peat can be decreased or increased by deep processing [5]. One of such scientific directions is thermal treatment, which causes a change in the group chemical composition of organic matter of peat [6]. The nature of such changes is determined (other conditions being equal) by magnitude and duration of thermal treatment of the material. When heated to temperatures above 150-180°C (in the absence or lack of oxygen) the peat begins to manifest the characteristic property of all biofuels – thermal instability. Its organic matter undergoes a complex transformation, the complex of which is called thermal decomposition, resulting in formation of solid, liquid and gaseous products [6]. It was established that by setting up certain parameters it is possible to obtain the maximum amount of thermal bitumen, which possess high hydrophobic characteristics. This gives the possibility to extract these products and further apply them as a coating film on an insulated material [7].

Thus, the aim of the study is to develop a method for hydrophobization of gypsum binder by organic components extracted from peat raw materials. The idea of the method consists in combining of two stages in the technological process of gypsum binder production: gypsum dehydrate calcination with simultaneous application of nano-films from peat bitumen onto the surface of its particles, which further isolates it from moisture.

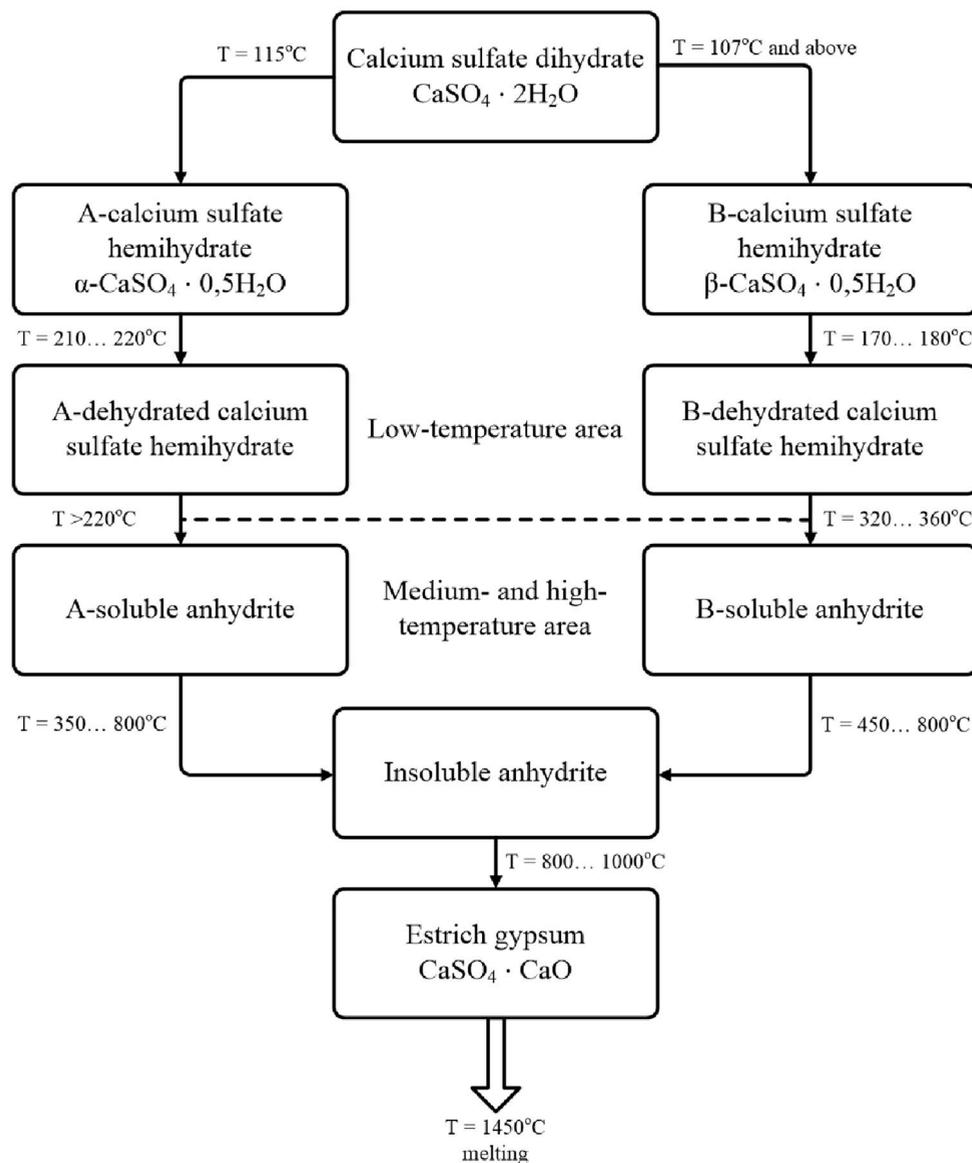
## 2 Method used

The main physical and chemical process in the production of gypsum binding materials is the disengagement of chemically bound water from the crystal lattice. The dehydration of calcium sulfate dihydrate occurs during heating according to the following chemical reactions:





The extracted products have different modifications depending on the reaction conditions [1-3]: calcium sulfate dihydrate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ),  $\alpha$ -calcium sulfate hemihydrate ( $\alpha\text{-CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$ ),  $\beta$ -calcium sulfate hemihydrate ( $\beta\text{-CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$ ),  $\alpha$ -dehydrated calcium sulfate hemihydrate ( $\alpha\text{-CaSO}_4$ ),  $\beta$ -dehydrated calcium sulfate hemihydrate ( $\beta\text{-CaSO}_4$ ),  $\alpha$ -soluble anhydrite ( $\alpha\text{-CaSO}_4$ ),  $\beta$ -soluble anhydrite ( $\beta\text{-CaSO}_4$ ) and insoluble anhydrite. Scheme and temperature ranges of the transition of calcium sulfate dihydrate to various modifications are shown in Figure 1.



**Fig. 1.** Scheme of modification formation conditions of calcium sulfate in the anhydrous and the hydrated forms

In normal conditions gypsum dihydrate is a thermodynamically stable solid-phase system. The free energy of the system is minimal, which allows it to be in a balanced state.

During thermal exposure there occurs separation of water molecules. This process changes its balanced state. The major product in this case is gypsum hemihydrate, the specific modification ( $\alpha$ - or  $\beta$ -modification) of which depends on the magnitude and duration of the heat treatment.

Hemihydrate calcium sulfate can be quite rarely found in pure form in nature.  $\alpha$ -calcium sulphate hemihydrate, in its turn, is formed by thermal exposure ( $T = 97-115^{\circ}\text{C}$ ) to gypsum dihydrate in an aqueous medium, saturated steam, and in a number of salt solutions [1] in accordance with the mechanism (1). That is, it is necessary to create an environment in which liquid droplet moisture will be released from gypsum dihydrate. Later on, the gypsum will start to crystallize in large, dense or transparent prisms or needles.

Next gypsum modification ( $\beta$ -calcium sulfate hemihydrate) is formed by heating gypsum dihydrate at  $T = 100-160^{\circ}\text{C}$  under normal conditions and under evaporation of moisture in the superheated steam state. This type of gypsum represents the smallest aggregates of not distinct crystals. Owing to such a process structure of the particles attains a developed inner surface. Specific surface of  $\beta$ -calcium sulfate hemihydrate is 2-2.5 times higher than the one of  $\alpha$ -calcium sulfate hemihydrate.

The speed of setting of  $\alpha$ -hemihydrate calcium sulfate when mixed with water is lower than the one of  $\beta$ -hemihydrate modification, which conversely has a higher hydration rate, since it has a larger specific surface of the particles [2].

With increasing treatment temperature on  $\beta$ -hemihydrate, up to  $170-180^{\circ}\text{C}$ , and on  $\alpha$ -hemihydrate up to  $200-210^{\circ}\text{C}$  remaining crystallization moisture removes and they move to  $\beta$ - and  $\alpha$ -dehydrated hemihydrates in accordance with the reaction (2). In this case the dehydration of the latter ones does not cause any visible structural changes.

Upon further temperature increase of  $\beta$ -dehydrated hemihydrate to  $320-360^{\circ}\text{C}$ , and of  $\alpha$ -dehydrated hemihydrate to  $220^{\circ}\text{C}$  and above there is a change of their crystal lattices and they convert into  $\beta$ - and  $\alpha$ -soluble anhydrites. The main differences of the obtained anhydrites from hemihydrate are in their higher water demand, quick setting and reduced strength [1]. A further thermal treatment in the range of  $360$  to  $800^{\circ}\text{C}$  on the above modifications of calcium sulphate results in complete rearrangement of the crystal lattice and, consequently, their conversion into insoluble anhydrite. This formation is very poorly soluble in water, and its solution almost does not set and harden.

In the next temperature range ( $T = 800-1000^{\circ}\text{C}$ ) insoluble anhydrite form decomposes into calcium oxide, oxygen, and sulfur dioxide. The product (Estrich-gypsum) obtained in these parameters includes insoluble anhydrite and small amounts of calcium oxide (2-3%).

In industry, the thermal treatment on the dihydrate gypsum is performed for 1-2 hours in special boilers with constant stirring. Generally, the maximum temperature of the material at the time of discharge from the boiler, depending on properties of raw materials and requirements to mineral binder, is in the range of  $140-180^{\circ}\text{C}$ . The process is divided into three stages. The first phase lasts about 20 minutes. During this time the temperature slowly increases from  $80$  to  $120^{\circ}\text{C}$ , which corresponds heating of the powder from the temperature at charging stage to the temperature of the beginning of intensive dehydration of gypsum. In the second stage the powder is kept for 30 minutes at the temperature of  $120^{\circ}\text{C}$ . This stage is characterized by intensive occurring of material dehydration with the removal of crystallization water. In the final third stage, the duration of which is 35-40 minutes, the temperature rapidly rises to  $180^{\circ}\text{C}$ . Dehydration intensity is lowered at the same time. After cooling, a ready-to-use material, semi-aquatic (building) gypsum, is produced.

The peculiarity of physical and chemical properties of raw peat is caused by its composition that includes a large number of different groups of chemical compounds [8]. However, most of them relate to hydrophilic components (humic and fulvic acids, cellulose,

lignin) and only a minor part comprises hydrophobic compounds: bitumen consisting of waxes, paraffins, oils and resins [7].

Theoretical basis for the creation of hydrophobizing additives on the basis of peat is studies of Russian scientists [9-11] that identify changes in the chemical group composition of peat upon its thermal treatment. It is known that upon drying of natural and (or) artificial peat it undergoes irreversible changes that lead to a significant decrease in water absorption capacity [12]. Moreover, the nature of such change depends on the quantity and duration of thermal exposure to the organic matter.

Thus, it is determined that upon heating peat up to the temperatures of 200-500°C and higher, in the latter it is significantly increased the content of hydrophobic substances compared to the source (native) peat. However, the main objective of the research is to provide such a method which will utilize not only the final hydrophobic materials obtained from peat, but also intermediate liquid and gaseous substances released upon its thermal decomposition.

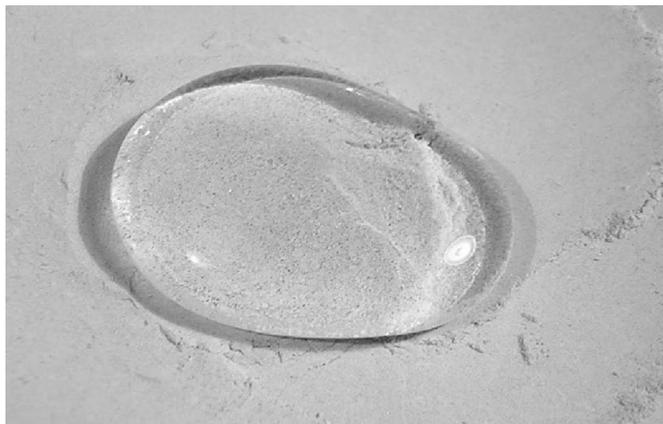
Based on the analysis of different methods for obtaining hydrophobic additives based on organic and mineral materials, there was developed a method for a water repellent processing of mineral binding powders by an organic peat-based additive [4].

The method of the hydrophobic modification of mineral dispersed materials by native and thermogenic bitumens, extracted from peat, was developed in relation to cement [7, 13]. Cement is mixed with a semi-finished peat additive with particle size of about 20-70 microns. Bog and mud peat with a medium decomposition level is used as an organic raw material. Preference is given to bituminous types of peat.

Further, heat treatment (activation) of the organo-mineral mixture is conducted at temperatures of 150-300°C. The concentration of peat component in cement enables to conduct the process even in the presence of oxygen in the air without the risk of ignition of the organic part. When treated thermally the organic matter of peat decomposes forming additional hydrophobic components. Water vapor and volatile matters remove themselves from the mixture at the initial stage of thermal decomposition. Hydrophobic pyrolysis products, primarily bitumen compounds, are sorbed in the form of thin films on the particles of mineral cement grains.

Image analysis of the Portland cement particles before and after thermal application of bitumen films on them allows to detect quality changes in distribution of chemical elements on the surface after the processing [4]. An extremely high carbon content, which is originally not included in the composition of cement clinker and gypsum, demonstrates presence of the organic film on the surface of the cement grains.

When implementing the developed method, hydrophobic coatings appear from the fluid resin products of peat organic matter pyrolysis on the cement particles and prevent them from wetting (Figure 2).



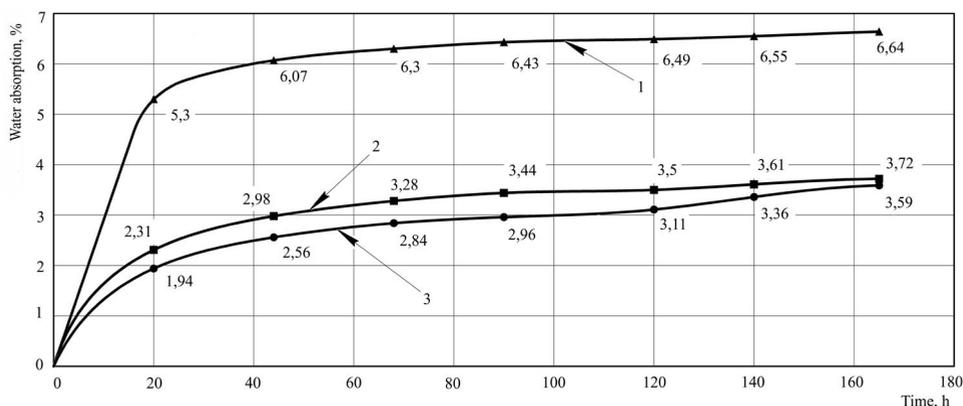
**Fig. 2.** Hydrophobicity test of the modified mineral binder: water droplets on the cement surface

The effectiveness of this hydrophobization method is high – we noted the increase of cement water-wetting time, regulated by GOST (Russian State Standard) No. 10178-85. When mixing the mortar, the mechanical action breaks continuity of the hydrophobic coating, which leads to its normal hydration and hardening.

### 3 Results & Discussions

Use of the method in the presented way in cement industry is extremely problematic due to a number of technological and economic issues. It requires adaptation to existing processes, or their minimal change. At the same time, the developed method can be well adapted to the process of production of gypsum binder. Basic parameters (temperature, time, presence of oxidation agents, etc.) of gypsum calcination technology [1, 2] meet the basic parameters of the hydrophobic modification process [7]. Experiments on calcination of gypsum dihydrate with peat hydrophobizers at  $T = 180-200^{\circ}\text{C}$  completely confirm this assumption. Optimization of the quantitative composition of peat additives allowed getting hydrophobically modified gypsum binder with low sorption capacity for water vapor and high strength.

Simulation of experimental gypsum binder storage under 100% relative humidity indicates that at a concentration of 2.1% additive there is a decrease in water vapor absorption of the modified materials by 2 times (Figure 3).



**Fig. 3.** Decrease in speed and capacity of water vapor sorption during storage of gypsum binder under 100% relative humidity: 1 – control sample; 2 and 3 with 1%- and 2%-additive, respectively

Moreover, increasing of the additive concentration does not result in a proportional decrease of water vapor absorption. This confirms the hypothesis that a protective barrier for the water molecules is a continuous bitumen film released during thermolysis of organic matter of peat and applied to the surface of the gypsum. Under these processing conditions the gypsum particles may keep per unit area of only the amount of bitumen which is determined by the energy of its interaction with the mineral surface. Most probably, the numerical value of the film thickness of the modified gypsum particles surface will be in the same range as that of the previously set for cement (11-22 nm) [13].

Peat is an inherently good organic binder which activity increases with the degree of mechanical dispersion. It is usually attributed to colloidal capillary-porous systems hardening due to coagulative structure formation upon drying [14, 15]. This feature is widely used in the production of various kinds of molded materials based on peat [16]: extruded fuel pellets or sod peat, peat-mineral fertilizers, insulation boards, spherical adsorbents [18] and other products. The mechanism of gypsum hardening is based, in its turn, on the reactions of hydration and occurs in three stages. That is, mineral binder and peat component do not chemically react with each other. If there are any chemical reactions, they may dominate and effect on the interaction of components only with relatively high concentrations of organic additives.

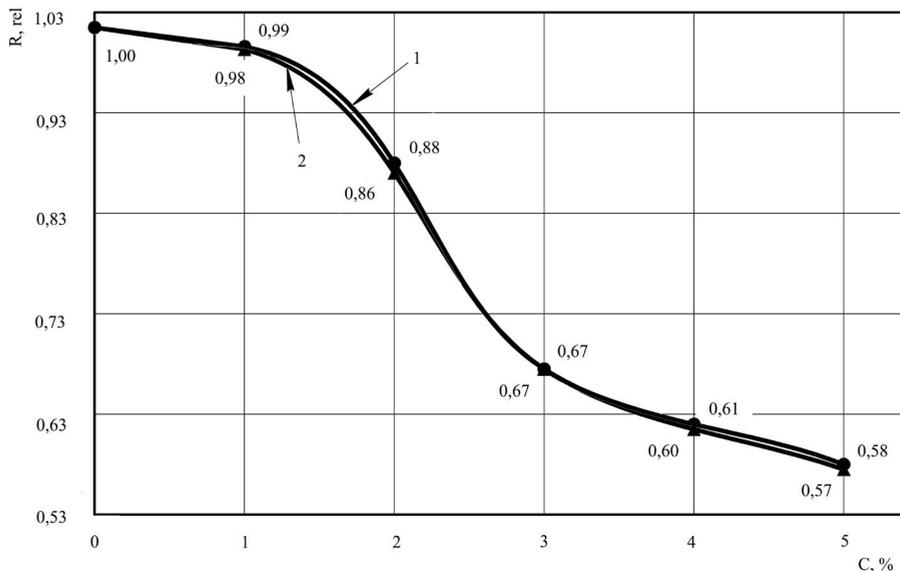
Proceeding from this it is possible to create building materials and constructions based on gypsum binder hydrophobically modified by peat additives the strength of which will not be lower than the one of control samples. However, it should be kept in mind that high strength properties can be achieved only by optimization of particles size, concentration of the hydrophobically modifying component and suppressing air entrapment [1]. In this case, there will be achieved a high hydrophobicity of the material that will not lower its strength.

For example, for Portland cement, use of mud-peat as a basic raw material for obtaining hydrophobic additives shows that there is a significant decrease in the strength of the samples only with the concentration of more than 2% of the mass of mineral binder. At the same time with 1%-content of an additive based on high-moor peat with the degree of decomposition  $R_t = 25\%$  it is observed a slight increase of flexing and compression strength [4].

The chart in Figure 4 shows the dependence of relative strength,  $R_{rel}$ , on peat additive concentration,  $C$

$$R_{rel} = R_{max} / R_i = f(C), \quad (3)$$

where  $R_{max}$  – maximum strength of the control sample (no additives) with uniaxial compression, MPa;  $R_i$  – experimental sample strength, MPa.



**Fig. 4.** Dependence of strength of gypsum binder experimental samples on concentration of organic additive based on peat: 1 – bog peat; 2 mud-peat

Dependence analysis (3) shows (Figure 4), that at a concentration of the peat hydrophobizing additive of 0.5-1% there is no critical decrease in strength characteristics as well as there is no increase in the setting time of gypsum samples. But at the same time, its storage time increases significantly without activity loss, also under adverse conditions. When the concentration of the organic component is of more than 1.5-2%, there is a decrease in the strength of gypsum, an expected negative factor. The strength reduces due to the decrease in the number of contact interactions in gypsum, caused by defects in its structure due to the presence of an organic component.

Despite high hydrophobicity of the obtained mineral binders, upon intensive mechanical stirring the hydrophobic bituminous films are «torn off» from the surface of the gypsum particles and are distributed throughout the volume of the mortar. Consequently, together with solid products of thermal degradation of organic matter of peat they create a "protective barrier" from moisture penetration into the sample. The effectiveness of this «barrier» depends on how evenly and orderly hydrophobic components are distributed in the solution.

Electron micrographs of cement stone [13] revealed fragmentary chaotic distribution of its organic components on the structural elements. Size of hydrophobic entities during zooming of individual sections ranged from 500 nm to 10 microns. However, even such a discrete distribution gives a sustainable hydrophobic effect on the surface of the hardened mortar – water does not penetrate into the sample. This does not occur even with the presence of open pores, which could potentially serve as moisture-conducting channels. Drops of water on the surface of the modified cement sample may be retained long enough. Moreover, wetting angle magnitude is substantially higher 90°, which indicates a high hydrophobization of the material surface [17].

It is expected that a secondary effect from the use of hydrophobically modified gypsum binder can be a significant reduction in moisture permeability and moisture capacity of solidified solution by making their structural elements water-repellent. For example, when experimental samples of hydrophobic cements were completely submerged into the water,

moisture absorption speed and water absorption capacity decreased by 2-3 times in comparison with the control samples [4].

Preliminary studies revealed that the developed method can be successfully applied also for hydrophobization of various kinds of bulk mineral and organic materials: lime, sand, clay, nitrile butadiene rubbers and so on, which opens up new directions for its use in other industries. At present, the authors conducts successful experiments to expand the raw material base for obtaining hydrophobic modifying agents. Good results are shown by peat subjected to self-heat, organic sapropel, wood residues extracted from peat deposits, industrial wood waste, and especially boghead coal used for this purpose. This is due to the conditions of formation of sapropelite coals from water-weeds residues, rich in fats. Their characteristic feature is the extremely low hygroscopic property (2-5%). When boghead coals are extracted with the alcohol-benzene mixture they disengage up to 10-12% of organic compounds: fatty acids, anhydrides, ketones and hydrocarbons. Accordingly, the organic matter of sapropelites is a macromolecular compound having a linear-condensed structure of polyesters type and comprising interconnected relatively long methylene chains and cycles. Because of a large number of hydroxyl and carbonyl groups in boghead coals there are preconditions for the formation of hydrogen bonds. Furthermore, when evaluating the prospects of using this material in hydrophobization processes an important role should be given to the fact that its organic matter has a relatively low thermal stability.

## 4 Conclusions

Thus, the results of the study allow to develop a technology for the production of gypsum binder hydrophobically modified by peat additives. The proposed method is completely adapted to the processes currently used in the production and do not require any technological equipment changes. Its use in the proposed form would not lead to an increase in the modify product cost, as the price of the semi-finished hydrophobic peat product equals to the cost of the source raw gypsum.

## References

1. L. Sycheva, *Glass and Ceramics*, **50**, 9-10, 440 (1994)
2. V. Korovyakov, *Rossijskij Khimicheskij Zhurnal*, **47**, 4, 18 (2003)
3. H. Fischer, B. Vtorov, *ZKG International*, **55**, 5, 92 (2002)
4. O. Misnikov, *Mires and Peat*, **18**, 1 (2016)
5. A. Afanas'ev, A. Boltushkin, *Colloid Journal of the Russian Academy of Sciences: Kolloidnyi Zhurnal*, **58**, 2, 139 (1996)
6. Y. Kosivtsov, K. Chalov, Y. Lugovoy, E. Sulman, A. Stepacheva, *Chemical Engineering Transactions*, **45**, 667 (2015)
7. O. Misnikov, *Theoretical Foundations of Chemical Technology*, **40**, 4, 423 (2006)
8. N. Gamayunov, B. Maslennikov, *Eurasian Soil Science*, **24**, 7, 32 (1992)
9. A. Afanas'ev, A. Efremov, *Theoretical Foundations of Chemical Engineering*, **45**, 1, 120 (2011)
10. Y. Navosha, S. Prokhorov, V. Strigutskiy, A. Tomson, *Eurasian Soil Science*, **24**, 5, 1 (1992)
11. K. Chalov, Y. Lugovoy, Y. Kosivtsov, M. Sulman, E. Sulman, V. Matveeva, A. Stepacheva, *Bulletin of Chemical Reaction Engineering and Catalysis*, **11**, 3, 330 (2016)

12. N. Gamayunov, V. Mironov, D. Stotland, Kh. Shebab, Colloid Journal of the Russian Academy of Sciences: Kolloidnyi Zhurnal, **56**, 3, 342 (1994)
13. O. Misnikov, Polymer Science. Series D, **7**, 3, 252 (2014)
14. A. Afanas'ev, S. Gamayunov, O. Misnikov, Colloid Journal, **61**, 3, 274 (1999).
15. N. Gamayunov, S. Gamayunov, Eurasian Soil Science, **38**, 3, 297 (2005)
16. P. Bel'kevich, L. Chistova, R., L. Rogach, M. Sobol, Solid Fuel Chemistry, **14**, 4, 125 (1980)
17. E. Bryuzgin, V. Klimov, O. Dvoretzkaya, L. Man', A. Navrotskiy, I. Novakov, Russian Journal of Applied Chemistry, **87**, 8, 1119 (2014)
18. N. Gamayunov, B. Maslennikov, Y. Shul'man, Eurasian Soil Science, **24**, 4, 122 (1992)