

# Scientific basis of a new method for hydrophobic modification of mineral binders using peat products

O. Misnikov

Department of Geotechnology and Peat Production, Tver State Technical University, Russian Federation

---

## SUMMARY

This study deals with the issue of caking of mineral binding materials during storage and transportation. The author conducted a critical analysis of known methods for the protection of cement from exposure to moisture and water vapour. Common disadvantages of these methods are their low effectiveness and complexity of use in industrial and domestic environments. This article introduces a new method for hydrophobising construction materials using peat, which achieves high water repellency in the modified materials with relatively low expenditure on organic materials. The author proposes film coating of the mineral particles of dispersed hydrophilic materials as a protection mechanism against their undesirable exposure to moisture during storage. The insulating film consists of hydrophobic products (bitumens) released during thermal decomposition of the organic matter in peat. The estimated thickness of the bitumen film is about 12 nm and it does not adversely affect the flow properties of the powder. A model of the formation of film coatings on mineral particles is provided and their elemental chemical composition is determined. It is shown experimentally that the modified hydrophobic cement is protected from exposure to liquid vapours, and optimal values of organic component concentrations in the dispersed mineral matter that do not reduce the strength of cement mortar are identified.

**KEY WORDS:** cement, film coating, hydrophobic material, hydrophobisation effect, peat bitumen

---

## INTRODUCTION

A negative property of various organic and mineral materials that are used in industry and everyday life is their susceptibility to caking (loss of their ability to flow) during storage. Caking results from physical and chemical processes occurring on particle surfaces which lead to phasic contact interactions. It is very often accelerated by the presence of water vapour in the environment. This is especially relevant to the storage of mineral binding materials used in construction (cement, gypsum, lime) and their composites (dry mortars), mineral fertilisers, fire extinguishing powders, *etc.* For instance, cement absorbs water vapour and carbon dioxide even if it is stored under conditions of low relative humidity (Volzhenskiy *et al.* 1979, Pashchenko *et al.* 1985, Gorchakov & Bazhenov 2012). This results in the formation of surface hydrates and calcium carbonate, which reduce its strength in construction materials by 20–30 % within 3–6 months. Gypsum binder also loses 30–50 % of its activity when stored for three months (Ferronskay 2004). Excessive physical and chemical deterioration of mineral binders occurs under

conditions of high relative air humidity.

There are several established methods for increasing the water repellent properties of dispersed mineral materials (Khigerovich & Baier 1979, Pashchenko 1987), which can be divided into two main groups according to their effects. The first group includes additives that have inherent hydrophobic characteristics. These ‘hydrophobic additives’ are obtained from animal and plant raw materials as well as from some minerals. The second group, called ‘hydrophobising additives’, includes materials and chemical compounds that do not possess inherent hydrophobic properties but acquire them when interacting with mineral binders.

Fats, oils and many other organic compounds, which are widespread in nature and have hydrophobic properties, have long been used in the construction industry. The Ancient Romans used lard and clotted milk or animal blood as hydrophobisers for air-hardening lime (Khigerovich 1957). In Ancient Rus’ curd mass, cereal chaff, ground flax seed and spruce bark extract were used for these purposes (Jung 1949). There is also technical information in scientific literature from the first half of the twentieth century on the industrial

production of hydrophobic cement by addition of whale oil and peanut butter.

Natural properties of fine coals and oil shales have also been used to hydrophobise mineral binders. One example proposed the addition of fine boghead coals at a rate of about 10 % of the binder's total mass to prolong the shelf life of cement (Afanasiev 1941). However, when this cement was used, it was necessary to separate out the additive as it would otherwise reduce the strength of the construction material.

Common shortcomings of the hydrophobisation methods mentioned above are low efficiency and, consequently, a need for high concentrations of the organic additives. In the middle of the twentieth century scientists started to develop methods for deep processing of organic raw materials based on hydrophobic plasticising materials or industrial waste created, for example, during the purification of soap stocks such as flax, hemp, sunflower, cottonseed and other oils. The outcome was that emulsified soap stocks proved effective as hydrophobising additives for construction materials. Some sources (Butenco & Luginina 2004) remark on the emergence of sustainable hydrophobic properties in cement modified with soap stocks but do not explain the mechanism by which experimental samples of mineral binders hydrophobised in this way gained in strength.

The use of hydrophobising additives obtained from products and waste materials of raw oil refining has become widespread. These hydrophobic-plasticising surface-active agents are divided, according to their production methods, into the following groups (Khigerovich & Baier 1979): synthetic fatty acids and their bottom products; modified bottom products of synthetic fatty acids; oxidised petrolatum; and naphthenic acids and their salts. The main feature that all surface-active hydrophobising agents have in common is an asymmetrically-polar molecular structure. This explains their amphiphile nature, *i.e.* their ability to simultaneously manifest hydrophilic and hydrophobic properties. The molecule consists of polar hydrophilic (COOH, COONa) and hydrocarbon (long hydrocarbon radical) parts. During interaction with the surface of a processed material the polar group binds strongly to the surfaces of the cement particles and aggregate grains that contain calcium ions, while hydrocarbon radicals turn outward. Surface-active hydrophobic additives are typically acidic, so the adsorption process is often accompanied by their chemical reaction with calcium ions in the cement, *i.e.* chemisorption of the surface-active agent's

molecules occurs. Thus, a water-repellent layer is formed around the cement particles and it becomes more difficult to moisten.

Besides the compounds mentioned above, a number of other materials are in widespread use for the production of hydrophobic and hydrophobising additives for construction materials, including: bitumens (Bel'kevich *et al.* 1977, Bel'kevich *et al.* 1985), organosilicon liquid (Sednev & Savchenko 2011), wood pitch, abietic resin and other products of chemical processing (Bryuzgin *et al.* 2014, Kunin & Lapshin 2015).

When considering the hydrophobising action of such additives, their tendency to reduce the cross-sectional areas of pores and capillaries and cause clogging should be taken into account (Kosinov 2012). However, in most cases, pore clogging is a minor effect that plays a very small role in improving the properties of mortars and concretes, because surface-active additives are introduced in small dosages of 0.1–0.5 %.

To summarise the above analysis, the main constraints on the use of hydrophobic mineral binders and building materials are as follows:

1. If the concentration of hydrophobic additives with molecules of asymmetrically-polar structure is increased above 0.1–0.3 %, the hydrophobicity of the cement remains relatively low but the strength of mortars based on them is significantly reduced. For example, the current Russian State Standard (GOST) 10178-85 requires that cement with a hydrophobising additive should not absorb any water within five minutes of applying a drop of water to its surface (regular cement absorbs water almost instantaneously).
2. Whilst remaining impermeable to liquid water, the processed materials are not able to stop the penetration of water vapour.

The production of effective organosilicon compounds is expensive, and yet the results of much research on their use are somewhat contradictory. Therefore, despite the wide range of commercially available water-repellent compositions, there is currently a shortage of cheap, simple to use and at the same time sufficiently effective repellents for the building materials market. This article reviews the development, by the author, of a peat-based water repellent treatment for cement. The scientific case for deriving a suitable water repellent from peat is explained, a method for applying it to cement is described, and the performance of the product is investigated. Finally, possible future directions of this research are explored.

## THE POTENTIAL OF PEAT AS A HYDROPHOBISING AGENT

At first sight, the peculiar physical and chemical properties of raw peat make it an unlikely raw material for water repellent manufacture. It is composed of a large number of different groups of chemical compounds (Rakovskii 1949, Rakovskii 1959, Lishtvan & Korol' 1975, Lishtvan *et al.* 1983), but most of them are hydrophilic (e.g. humic and fulvic acids, cellulose, lignin) and only a few are hydrophobic (e.g. bitumen consisting of waxes, paraffins, oils and resins).

The theoretical foundation for creating hydrophobising additives from peat was established by Russian scientists (Rakovskii *et al.* 1959, Smol'yaninov & Maslov 1975, Bazhenov *et al.* 1999, Sulman *et al.* 2009, Lishtvan *et al.* 2012), who noted changes in the chemical composition of peat during thermal treatment. It is known that peat undergoes irreversible changes on natural and/or artificial drying that lead to a significant reduction in water absorption capacity (Efimova & Pukhova 2013). Moreover, the nature of this change depends on the temperature and duration of thermal exposure.

Many factors influence the nature of the processes that lead to peat developing hydrophobic properties, as well as the exact nature of these properties. Our present understanding is that the outcome is temperature dependent. When drying peat under field conditions (surface temperature 20–50 °C) with humidity ranging from ( $w_n = 75\text{--}80\%$ )

to ( $w_k = 40\text{--}45\%$ ), changes in hydrophobic properties are caused mainly by the sorption of air in the pore spaces within the structural elements of peat particles (Figure 1). Hydrophobicity is also caused, to a lesser degree, by minor physical and chemical changes at macromolecular level (oxidative processes during contact with oxygen in the air). Therefore, if peat dried by this method is put into water, the water will in time displace air and wetting of the material will occur. However, the original water absorption capacity of the peat will not be attained (Efimova & Pukhova 2013). When the drying temperature is increased to 105 °C (e.g. in laboratory determinations of water content or the first stage of industrial drying), there is further oxidation and the water-repellent properties of the peat increase.

These temperature ranges are of little interest in relation to the production of organic hydrophobising compounds from peat. In this context, the most promising approach exploits the distinctive thermal instability of peat. When heated to higher temperatures the organic matter in peat undergoes a complex transformation, termed thermal decomposition, in which new solid, liquid and gaseous products are formed (Rakovskii *et al.* 1959, Smol'yaninov & Maslov 1975) and significant quantities of hydrophobic substances that were not present in the source raw material appear.

Peat particles differ not only in chemical composition, but also in their physical properties. Experiments on peat carbonisation (Rakovskii *et al.* 1959) showed that, in the temperature range 150–

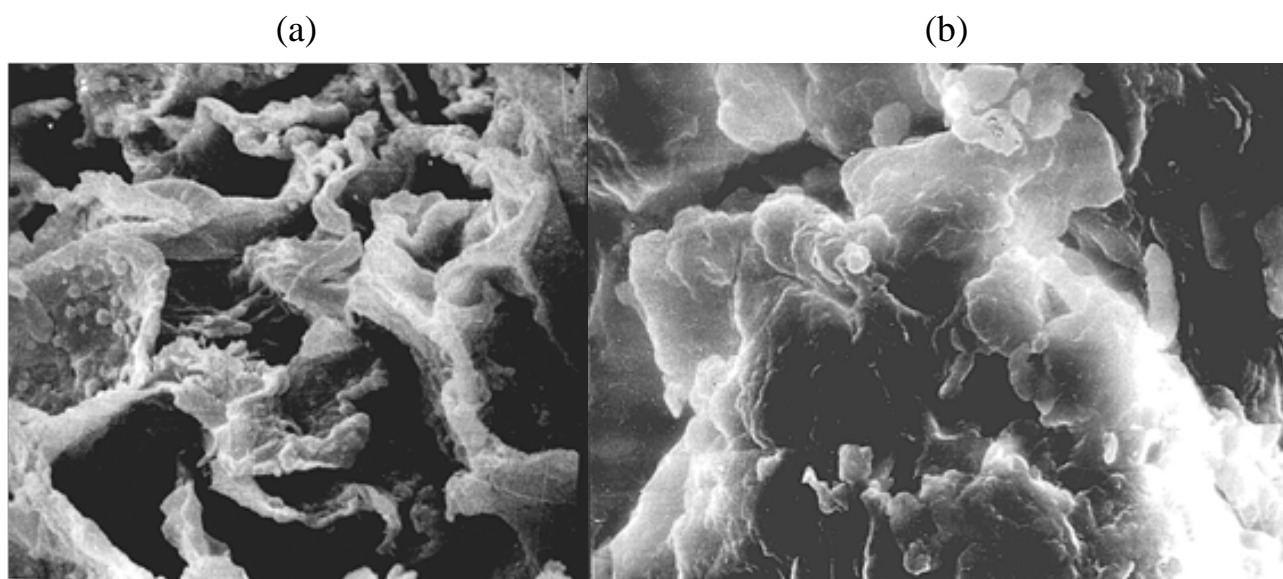


Figure 1. Scanning electron micrograph (SEM image) of the structure of a separate fragment of a peat particle. Left:  $\times 3,000$ ; right:  $\times 6,000$ .

500 °C, peat possesses plastic properties. These properties can be evaluated by measuring the indentation diameter of a ball under a specified constant load. As temperature is increased the indentation diameter increases to a maximum at temperatures of 280–320 °C, depending on the type of peat. In fact, peat under thermal exposure passes through a softening stage which results in condensation reactions of aromatic compounds. This means that the organic matter of peat consists of two physical parts, one of which melts whilst the other remains solid and does not change its aggregation state at these temperatures. The molten mass (created by the presence of bitumen resins, some water-soluble compounds and lignin) impregnates the infusible part, coats the particles and fills the spaces between them (Lishtvan *et al.* 1983). Maximum softening is observed at about 300 °C; then, if temperature is increased further, aromatic compounds condense resulting in solidification of the mass and char formation. These studies were a logical continuation of an analysis of processes occurring during the formation of lump coke from coal that was carried out in Germany by Agde & Lyncker (1930), who claimed that thermal treatment of coal releases ‘oily bitumen’ which determines the susceptibility of coal to sintering, as well as “solid bitumen” which imparts the material’s capacity to swell. They also found that both colloidal and gel forms of bitumen are contained in coal. Depending on the type of coal tested, the initial boiling point of oily bitumen was 130–140 °C, the melting temperature of solid bitumen was in the range 130–210 °C, and the decomposition temperature of the latter was about 10 °C above the melting temperature.

Very interesting data on the carbonisation of bitumen in different weakening admixtures with sea sand, pumice, diatomaceous earth and coke fines have been obtained by Lishtvan *et al.* (1983). These authors concluded that porous weakening admixtures increase yield and form dense durable coke. This occurs because the capillary effects introduced with dispersed mineral and organic components suck up the bitumen that is produced during thermal processing of peat and, due to a sufficiently high bond energy, can retain it for a long time. Great importance is attached to the role of oily bitumen in the carbonisation processes, since it lowers the melting temperature of all bitumen contained in the coal and acts as a solvent for its solid part during the initial stage of carbonisation.

During the development of various complex peat processing technologies (Tomson & Naumova 2009), gradual extraction of the required chemical

compounds was proposed. In one case, after extraction of bitumen, the residual organic matter was held at a temperature of 250 °C for two hours, after which it had acquired highly hydrophobic properties. This material was used as a filler in plastics, an additive for phenol-formaldehyde resins, *etc.*

Thus, it is now established that when peat is heated to temperatures of 200–500 °C and above, its content of hydrophobic substances is significantly increased compared to the source (native) peat. However, the main objective is to provide a method that will utilise not only the final hydrophobic product from the processing of peat, but also the intermediate liquid and gaseous substances that are released during its thermal decomposition.

## THE HYDROPHOBISATION OF CEMENT USING PEAT

### The peat-based treatment method

The above analysis of different methods for obtaining hydrophobic additives from organic and mineral materials led to the development of a method for water repellent treatment of mineral binding powders with an organic peat-based additive (Misnikov *et al.* 2004). The semi-finished additive is a finely dispersed organic substance obtained by grinding dried peat. Bituminous peat types are preferred.

Despite the relatively high hydrophobicity of the dried peat, straightforward mechanical stirring of the semi-finished organic additive with the mineral binding material does not result in formation of protective water-repellent films on the surfaces of the cement particles. During standard tests the peat-cement mixture remains on the water surface for some time (Figure 2a), then after 15–30 minutes the cement starts to moisten and eventually descends to the bottom of the container. In this case the organic additive remains on the surface (Figure 2b).

Therefore, the scientific challenges involved in achieving a stable water-repellent effect in an organo-mineral peat-cement composition included not only the extraction of organic hydrophobising compounds, but also their application onto the surfaces of the mineral particles of the cement. The application is conducted directly in the reactor where, as the liquid products of peat thermolysis are formed, they precipitate as water-repellent films (Misnikov 2006) on the surfaces of the mineral particles (Figure 3). This process is called thermal activation of the organo-mineral mixture. Since it is very difficult to separate the phases of

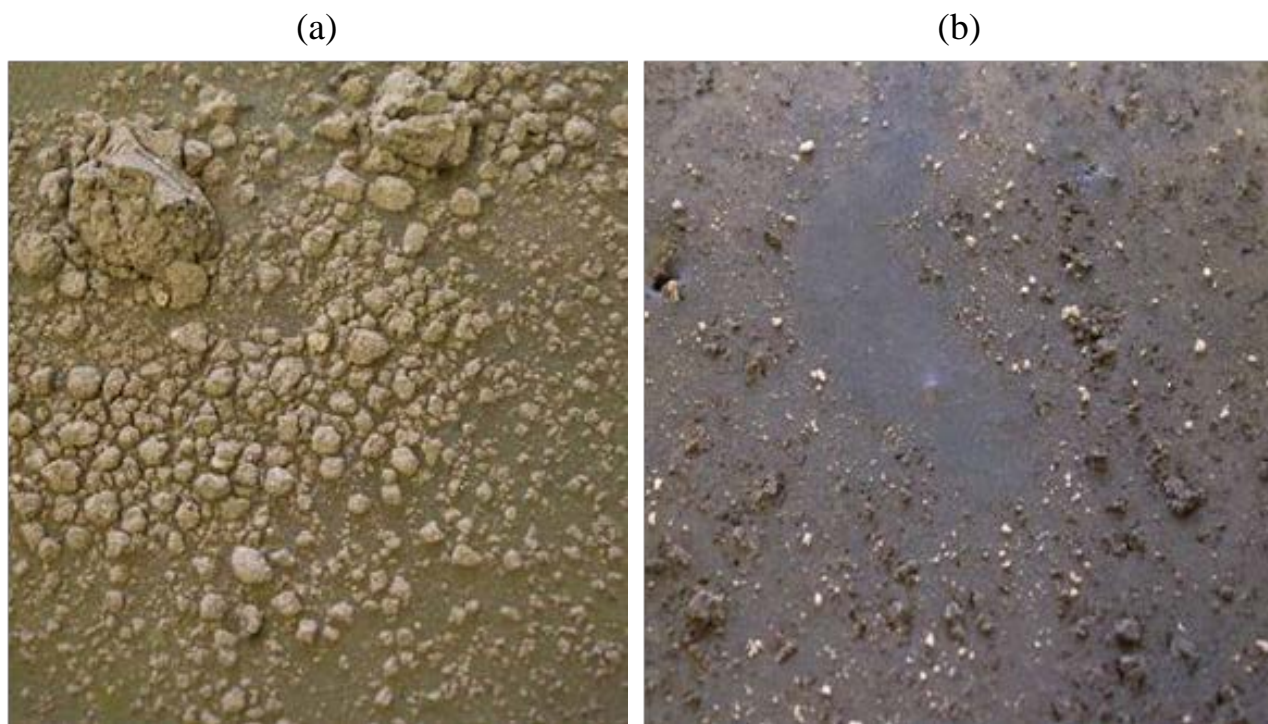


Figure 2. Separation of the two-component peat-cement mixture on a water surface: (a) beginning of the experiment; (b) 30 minutes after beginning of the experiment.

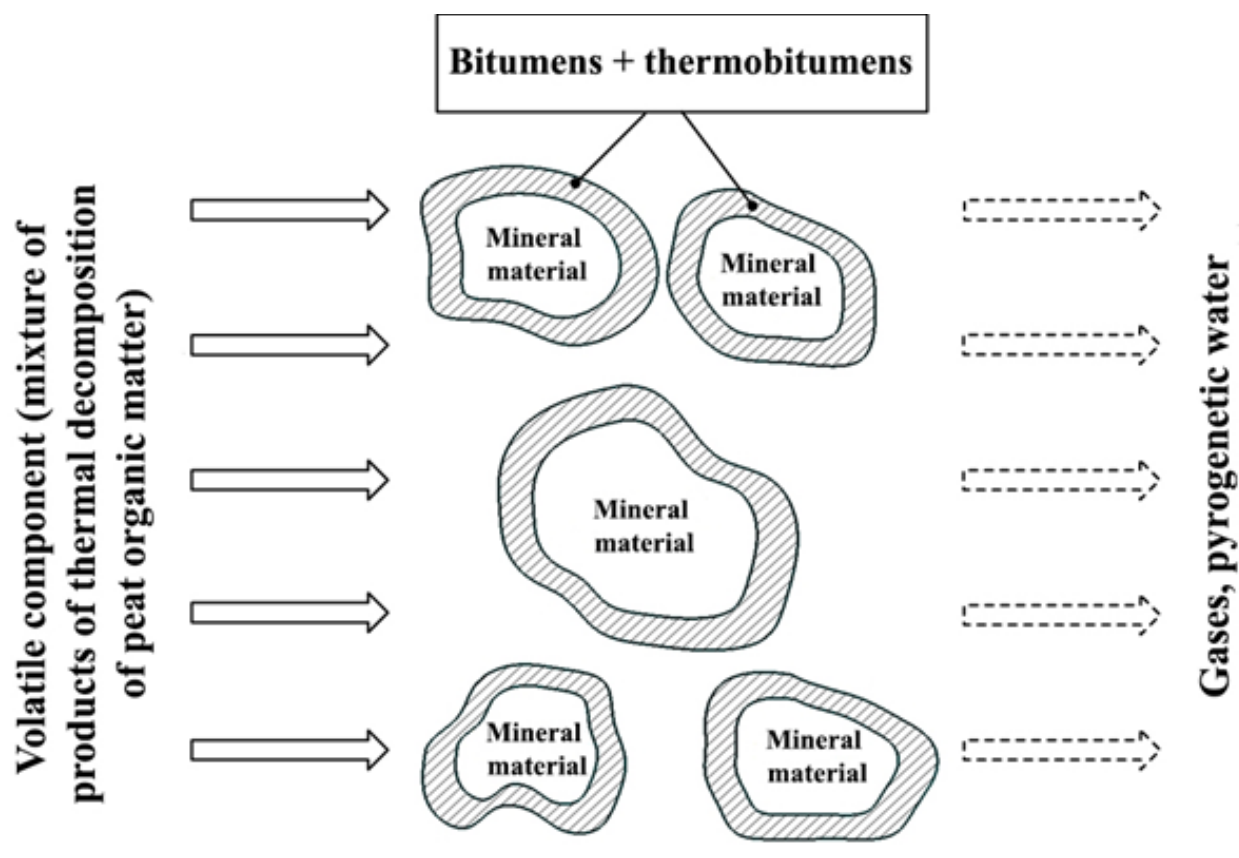


Figure 3. Model of hydrophobic film formation on grains of mineral binder.

disengagement of hydrophobic components from the peat and their application to the mineral particles, we can assume that they occur simultaneously. Additional grounds for this assumption can be drawn from the various temperature ranges over which the individual components of peat organic matter decompose during the heating process. The main mechanism by which protective films form on the hydrophilic surfaces of cement is physical adsorption of bitumens. Operational parameters (temperature, humidity, pressure, oxidiser-flow rate, *etc.*) of the thermal activation will depend on the type of mineral binding material as well as on the required final characteristics of the building material (Misnikov 2006). This study was carried out in aerobic mode with temperature range 180–250 °C.

For simplicity, the organic agent (peat) was left in the organo-mineral mixture after removal of hydrophobic components (Figure 4). The cement grains (white particles in the image) are no larger than 15 microns across. The dark particles of organic additive (on the right in the image) are considerably larger, at about 20 × 70 microns; and traces of layering from the thermal exposure, which led to the formation of numerous micro-pores, are clearly visible on their surfaces. The micro-pores allowed gaseous and liquid products of thermal decomposition to move outwards from the particle. It is noted that the strength of organic particles decreases considerably after thermal exposure, which leads to a prediction that they will undergo fairly rapid destruction (size reduction) while stirring to obtain mortars. This, together with the optimisation of concentration, minimises possible negative effects of the organics on the final product (cement mortar).

It is possible, in theory, to separate out the organic agent from the processed product after thermal activation, but this significantly complicates the entire process. So far this approach has been applied only to evaluate the thickness of the film coating the particles, which was about 12 nm (Misnikov 2014, Misnikov & Chertkova 2014).

### Characteristics of particle coatings

This hydrophobisation method is highly effective. Cement powder whose particles had been coated with hydrophobic films of sorbed liquid resinous substances and solid components of thermally activated peat (Figure 4) became so highly water-repellent (Figure 5) that the minimum time for moistening required by the Russian State Standard (GOST) 10178-85 was exceeded by dozens of times in almost all of the experiments conducted. This

suggests that the method is successful in forming continuous films of water repellent coating on the cement particles.

To build a completely objective picture of the coatings on the mineral particles, we carried out a series of experiments using a scanning electron microscope JSM-7001F with Schottky cathode (thermal field emission). This allowed the investigation of structural and chemical characteristics of solid samples that are suitable for study in high vacuum, in SEI, COMPO, TOPO and Shadow modes. Resolution on the reference Au sample in SEI mode was 1.2 nm. We conducted a further analysis for distribution of chemical elements in the range C to U, sampling at points (3 microns) within a line or area of scanning using an EDS-spectrometer.

Image analysis of Portland cement particles before and after thermal application of bitumen films allows quality changes in the distribution of chemical elements on their surfaces to be detected (Figures 6 and 7).

An extremely high carbon content, which is not detected in the original composition of cement, clinker and gypsum, demonstrates the presence of an organic film on the surfaces of the cement grains (a picture of the control sample is not provided because carbon is absent from its surface). Moreover, it is possible to encourage the deposition of carbon onto the surfaces of mineral particles with organic dust (e.g. from ambient air) as well as in the process of absorption of carbon dioxide by cement grains. However, in this case, the quantity should be minimal - less than the major chemical components of cement clinker (Ca, Si, O, Fe, Mg, Al). Analysis of the relative change in the content of elements along the scanning line (3 microns) revealed that the amount of carbon in the surface layer at the transition from one mineral grain to another increased by 3–9 times (Figures 6 and 7). The intensity of carbon distribution is comparable in magnitude to that of the basic elements of cement clinker (Ca, Si and Al). A special feature is the exactly opposite (relative to C) character of the content change of calcium and silicon, which decreases by 1.5–2.5 times. This is apparently due to the suppression of signals from these elements, or to an effect related to the occurrence of thermal reactions of partial decalcification and desilicisation of the surface layer in the presence of organic compounds. The content of aluminium hardly changes during processing (Figure 7).

Thus, electron microscopy confirms that a carbonaceous material is applied to the surfaces of the mineral particles.



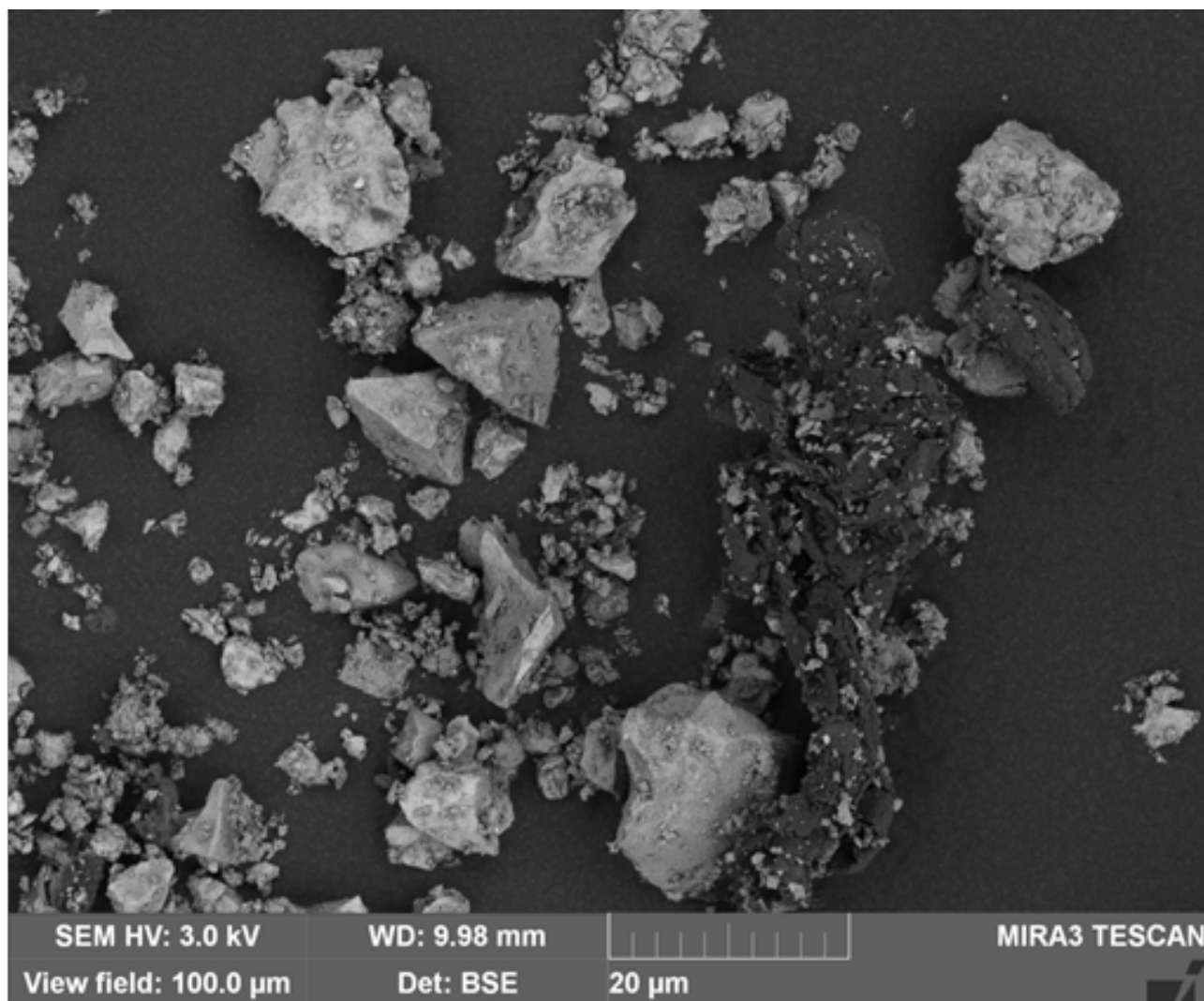


Figure 4. Electron micrograph of the organo-mineral mixture after thermal activation.

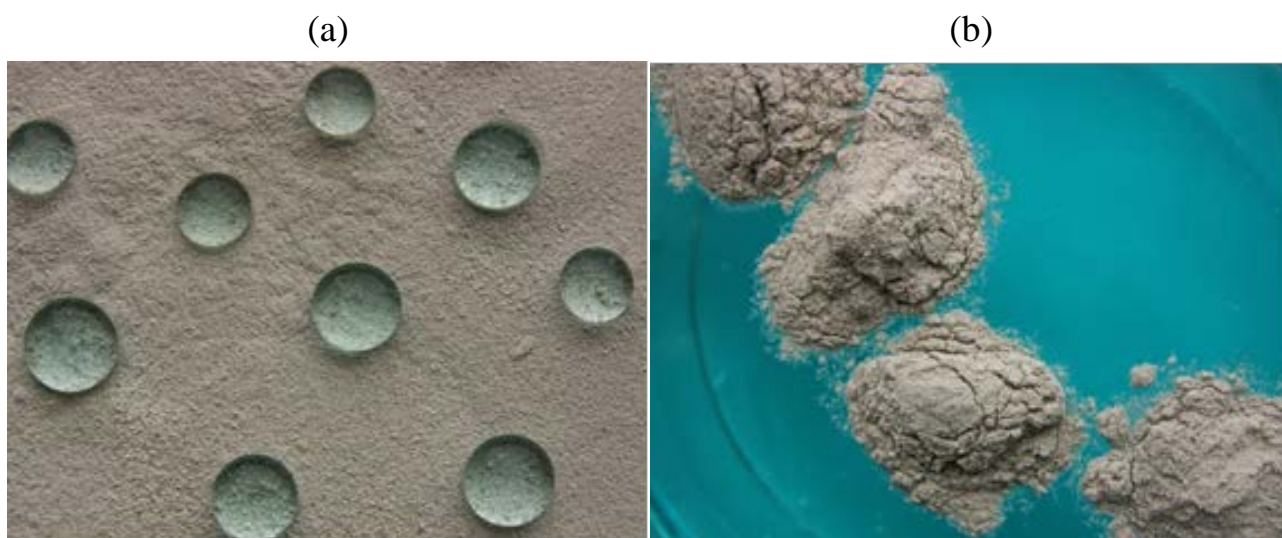


Figure 5. Hydrophobicity test of the modified mineral binder: (a) water droplets on the cement surface; (b) the powder floating on a water surface.

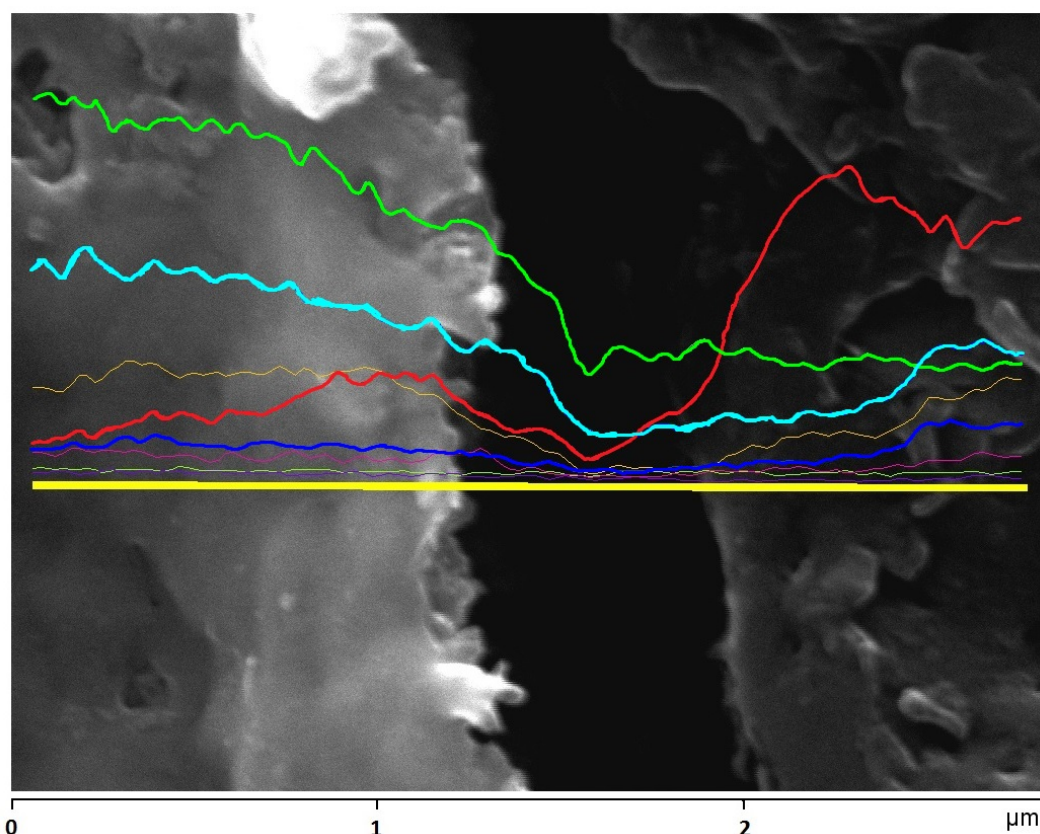


Figure 6. Electron micrograph of the surfaces of two cement grains with different degrees of hydrophobisation, showing the distributions of chemical elements (see also Figure 7).

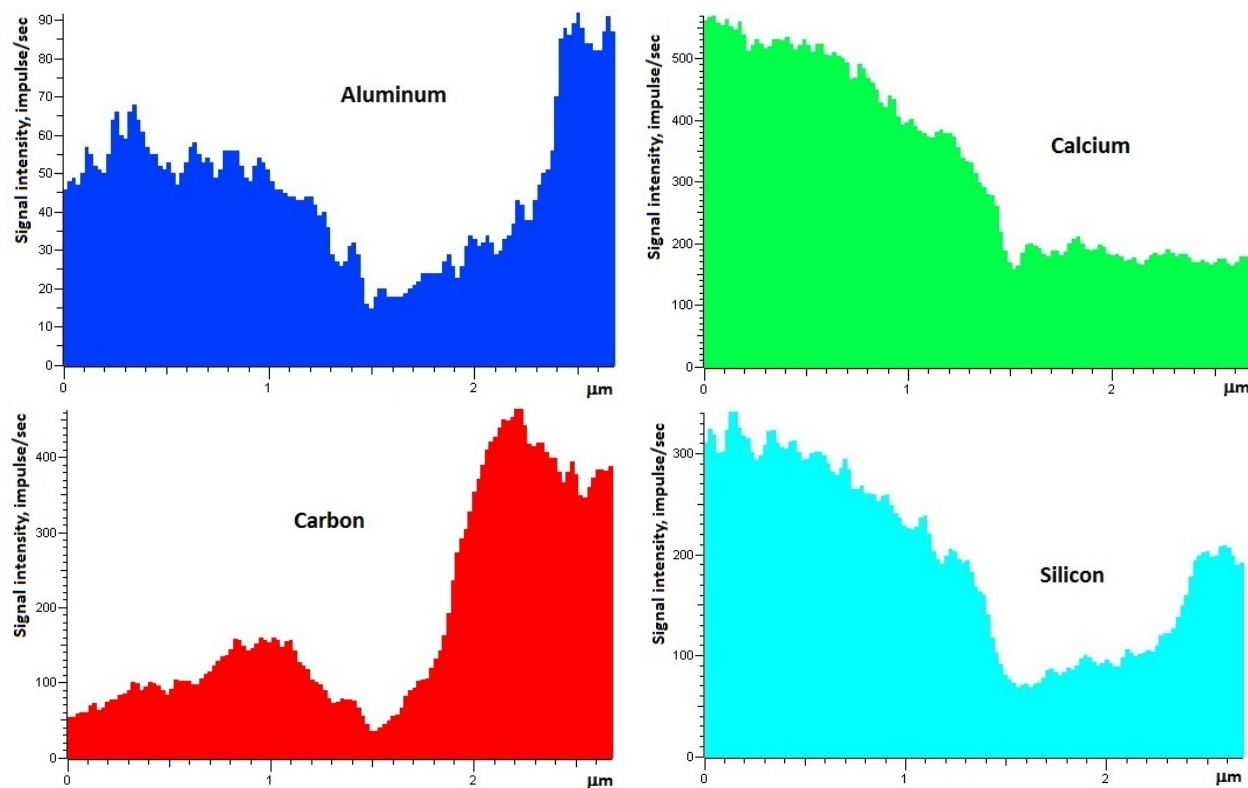


Figure 7. Distributions of the four most characteristic chemical elements on the hydrophobically modified cement particles in Figure 6. Colour coding as in Figure 6.



## PERFORMANCE OF THE COATING

### Exclusion of water vapour

As stated above, the isolation of mineral binding material from the effects of water vapour is particularly challenging, since liquid moisture can also gather on structures with discrete distributions of hydrophobic components. To exclude water vapour, continuous coating of the particles is necessary. Only in this case can it be guaranteed that the mineral binders will acquire increased shelf life without losing their physical and chemical characteristics.

It is known (Taylor 1996) that the interaction of moisture with cement powder has a chemisorptive character. Adsorption of moisture and its capillary condensation occurs during the first stage. Then cement components dissolve in the condensed moisture and the cement grains are covered with a layer of hydrates. Carbonation of lime which is disengaged during the hydrolysis of tricalcium silicate, and sealing of the hydrates film, also occur. After formation of the first film of hydrates the process does not stop, but rather continues owing to growth of microcracks and condensation of moisture within them. This process can continue until the cement is completely hydrated. Hydration of a binder stored in humid conditions reduces its content of active ingredients. Activity is also lost through deceleration of the reaction between cement grains and water arising through inhibition by films formed by hydrates.

Hydrophobisation using one of the "classical methods" (Khigerovich 1957, Khigerovich & Baier 1979) allows cement to be isolated from liquid water quite reliably, but carbon dioxide and water vapour freely penetrate the coating and react with the binder. Although the mass of water vapour penetrating to classically hydrophobised particles is significantly smaller than in control samples, it is nonetheless sufficient to reduce the activity of cement during storage. Khigerovich (1957) reports that the weight of hydrophobic cement stored in a humid atmosphere for 3–6 months increased by 2.5–3.5 %, while the weight of regular Portland cement increased by 6–14 % and its carbon dioxide content 8–12 times. Hydrophobisation was even less effective in the case of alumina cement, for which the mass increment was 6.4–14.4 % in hydrophobic samples and 18.3 % in the control. This confirms once again that the structure of protective coatings formed on cement grains using the method of M.I. Khigerovich are not continuous, but have an intermittent "reticulate" or "mosaic" structure that can be penetrated by water vapour.

In this study, in order to estimate the amount of water vapour absorbed by cement treated with peat, the following experiment was conducted. Samples of control and hydrophobically modified cements in petri dishes were placed over water in a desiccator and held at relative humidity  $\varphi = 100\%$  and temperature  $T = 20\text{--}25\text{ }^{\circ}\text{C}$  for 130 days. An analytical balance was used to determine weight increments during storage to an accuracy of 0.0001 g. The kinetics of water vapour absorption are shown in Table 1. The results for control and hydrophobically modified samples were almost identical on the first day. On the second day, the control began to gain moisture rapidly, and after seven days its vapour absorption reached 3.32 %. In the modified cements this value fluctuated around 1 %. Vapour absorption by the control sample increased to 26 % after 50 days then started to stabilise, increasing only slightly over the next 80 days. The nature of the absorption process indicates that about 25 % out of a total of 34.4 % of water vapour bonds chemically with mineral binders during the hydration process. The remaining water mass can be regarded as physically and chemically bonded, as it evaporates during drying of the material.

The modified cement samples were then taken from the desiccator and dried ( $T = 105\text{ }^{\circ}\text{C}$ ). During drying, the amount of adsorbed moisture reduced to 1.75–22 times depending on the concentration of the hydrophobic agent. The weight of the control sample reduced only from 34.4 to 25.5 % during drying, while the weight reductions of the hydrophobically modified samples were: (1 %) from 19 to 14.5 %; (2 %) from 2.66 to 0.012 %; (3 %) from 2.54 to 0.009 % and (4 %) from 2.25 to 0.006 %. After this the experimental cements almost completely recovered their properties and could be used in mortars without additional drying. The control sample, on the other hand, was completely hydrated cement. To restore its properties, high-temperature firing followed by fine grinding would be required. This experiment demonstrates that the mineral binder excludes water vapour, once again proving that the particle coatings are continuous.

### Effect on mortar strength

Peat is an inherently good organic binder whose activity increases with mechanical dispersion. This is usually attributed to hardening of its colloidal capillary-porous systems due to the formation of coagulative structures during drying (Afanasiev *et al.* 1999, Afanasiev & Efremov 2011). This feature is used widely in the production of moulded materials based on peat (Tomson & Naumova 2009) such as extruded fuel pellets or sod peat, peat-

Table 1. Kinetic dependence of water vapour absorption value by cement samples at a relative air humidity  $\varphi = 100\%$ .

Time, days	Water vapour absorption, (mass) %				
	Control	Hydrophobically modified by bog peat additive with concentration, %			
		1	2	3	4
1	0.95	0.64	0.85	0.76	0.93
2	1.1	0.77	0.75	0.86	1.00
3	1.27	0.82	0.73	0.89	0.95
4	1.64	0.84	0.73	0.91	0.94
5	2.11	0.86	0.78	0.86	0.96
6	2.53	0.89	0.81	0.84	1.00
7	3.32	1.06	0.9	0.94	1.04
14	8.55	1.21	0.93	1.07	1.07
21	14.01	1.34	0.99	1.02	1.05
35	22.53	2.48	1.39	1.14	1.29
49	26.95	4.29	1.63	1.37	1.33
70	29.65	7.48	1.95	1.61	1.54
100	32.1	12.7	2.29	1.89	1.79
130	34.4	19.06	2.66	2.54	2.25

mineral fertilisers, insulation boards, spherical adsorbents and other products. On the other hand, the mechanism of cement hardening is based on hydration reactions and hydrolytic dissociation (Taylor 1996). In other words, the mineral binder and peat components of a mixture do not react chemically with each other. If there are any chemical reactions, these may dominate and effect the intended interaction of components only when the concentrations of organic additives are relatively high.

On this basis it should be possible to create concrete mixtures and mortars, based on mineral binders that have been hydrophobically modified by peat additives, whose strength will not be any lower than that of unmodified materials. However, it should be kept in mind that high strength can be achieved only if particle size and concentration of the hydrophobically modifying component are optimised and air entrapment is suppressed (Batrakov 1998). In this case, high hydrophobicity of the material will be achieved without reducing its strength.

When hydrophobic additives are obtained from mud-peat there is a significant decrease in strength of the samples only when the concentration of additive 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 of flexing and compression strength is observed (Figure 8, Graphs 1 and 3).

To assess the effect of hydrophobic modification of cement on the properties of derived mortars after hardening, the structure of thin sections and cylindrical samples was studied in scanning electron micrographs. The effect of the modifying additives on the structure of the intergranular pore space was established by qualitative analysis of surface topography. The pore structure of the control samples was made up of localised cavities and dangerous micro- and macro-cracks (defects). In contrast, with relatively low concentrations of additives (up to 1 %), the structure was solid and almost without cracks. The intergrain spaces in all samples were filled with a mass of fine globules and plates.

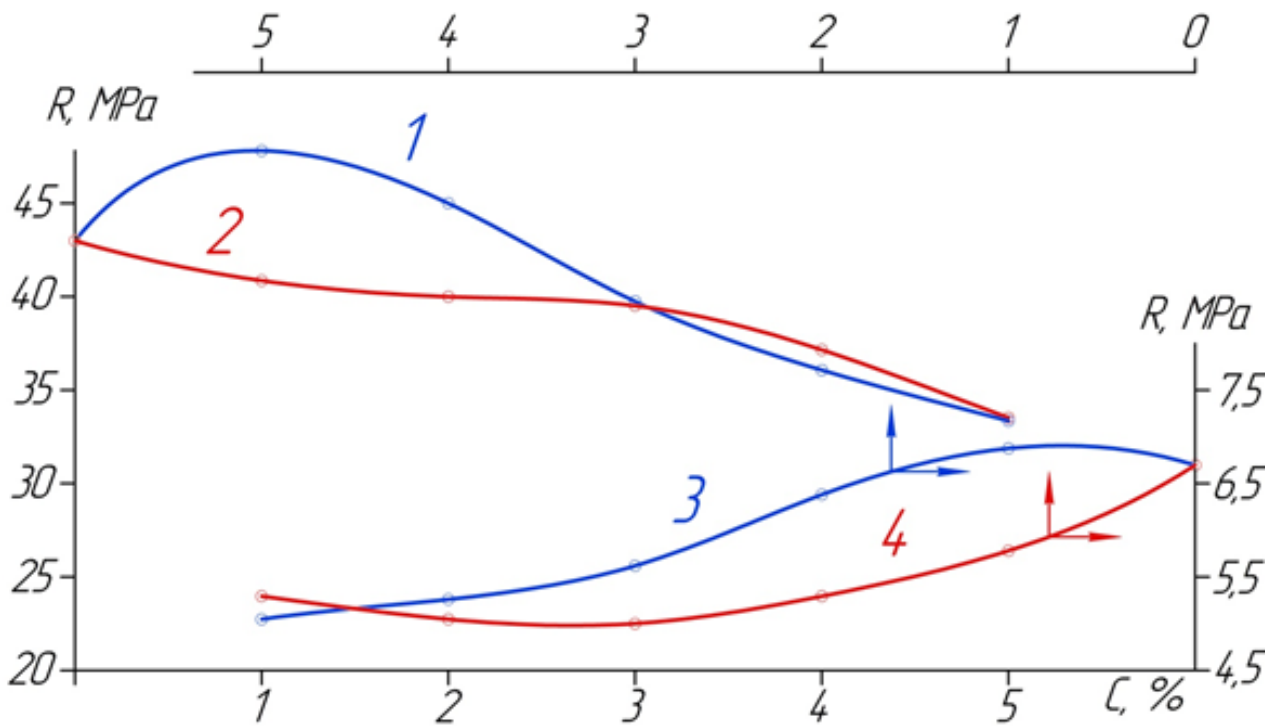


Figure 8. Dependence of strength  $R$  on the concentration of additives in compression (1, 2) and in flexing (3, 4) of samples of M-500 Portland cement (Belgorod city) with hydrophobically modifying additives derived from bog peat ( $R_t = 25\%$ ) (1, 3) and mud peat ( $R_t = 30\%$ ) (2, 4).

Fractographic studies revealed peculiar behaviours of the samples upon shearing. Grain size was large in the control samples, and fracture occurred along intergranular adhesions and defects. The structure of chips of the modified mortars was characterised by denser packing of cement particles on the surface of the filler (sand). Moreover, their degree of dispersion was significantly higher than in the control materials. As a result, the number of contacts increases and the physical and mechanical properties of the structure improve. Therefore, the effect of modifying additives creating hydrophobic "barriers" leads to lengthening of the period of cement setting by lowering the rate of cement hydration.

Despite the high hydrophobicity of mineral binders that was achieved, intensive mechanical stirring causes the hydrophobic bituminous films to be 'torn off' from the surfaces of the cement particles and distributed throughout the volume of the mortar. Consequently, together with solid products of the thermal degradation of peat organic matter, they create a 'protective barrier' against moisture penetrating into the sample. The effectiveness of this 'barrier' depends on how evenly the hydrophobic components are distributed in the solution.

Electron microscope images show a chaotic fragmentary distribution of organic components on the structural elements of the cement stone (Figure 9a). Zooming-in on individual sections at the given resolution shows that the hydrophobic formations (dark spots in Figure 9a) range in size from 500 nm to 10 microns. However, even such a discrete distribution gives a sustainable hydrophobic effect on the surface of the hardened mortar (Figure 9b). Water does not penetrate into the sample even when open pores, which could potentially serve as moisture-conducting channels, are present. Drops of water on the surface of the modified cement sample are retained almost indefinitely. Also, the wetting angle is substantially greater than  $90^\circ$ , which indicates high hydrophobisation of the material's surface.

Thus, a secondary effect of using hydrophobically modified cements is that the moisture conductivity and moisture capacity of hardened mortars, concretes and other building materials derived from them are significantly reduced by water-repellent properties imparted to their structural elements. When an experimental sample is fully immersed in water its absorption rate and the amount of water absorption are reduced 2–3 times compared to the control sample (Figure 10).

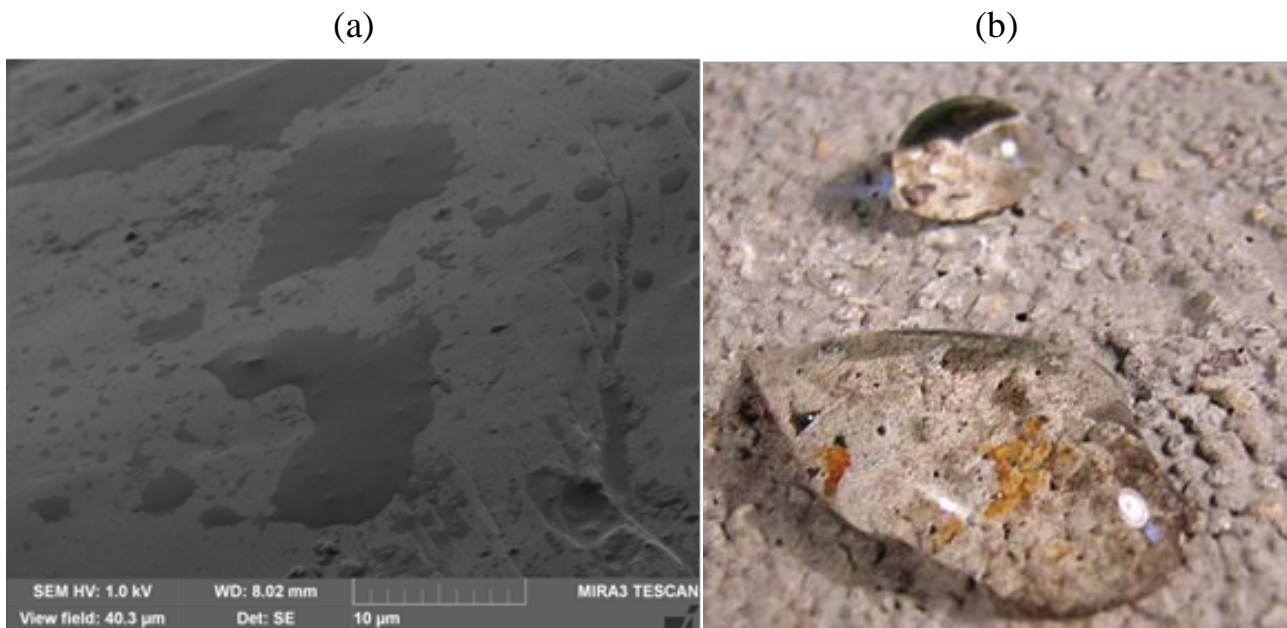


Figure 9. Images of (a) a fragment of cement stone with micromosaic distribution of hydrophobic compounds (electron microscope) and (b) the surface of hardened cement mortar (macrography).

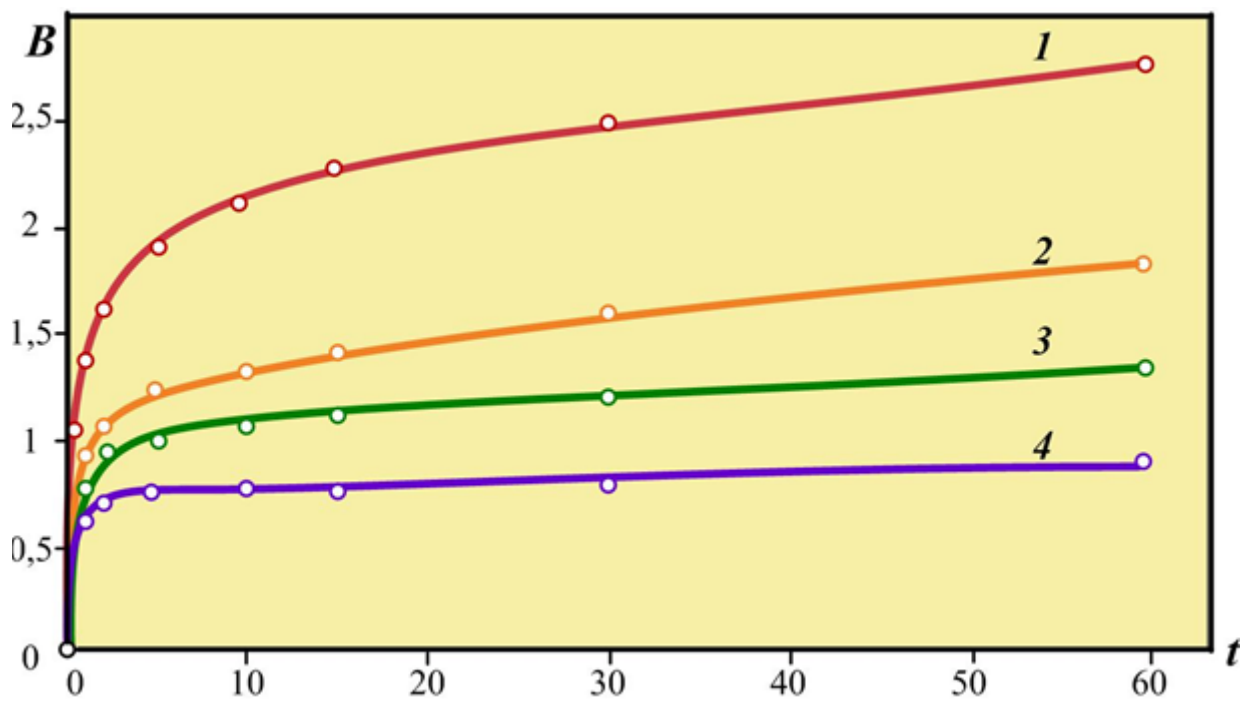


Figure 10. The dependence of water absorption  $B$  (%) on time  $t$  (minutes) for the control sample (1) and for samples of cements modified with hydrophobic additives obtained from bog peat ( $R_t = 25\%$ ) at concentrations of 1 % (2), 3 % (3) and 5 % (4).

## FUTURE DIRECTIONS

Preliminary studies indicate that this method can also be used for hydrophobisation of other bulk mineral and organic materials including lime, gypsum, sand, clay and nitrile butadiene rubbers,

which opens up substantial potential for applications in other industries. At present, the author is conducting successful experiments to expand the raw material base. Good results are shown by peat subjected to self-heat, organic sapropel, wood residues extracted from peat deposits, and industrial



wood waste, as additional sources of hydrophobic modifying agents. The especially promising performance of boghead coals arises from the fact that sapropelite coals are formed from the residues of water-weeds, which are rich in fats. Their characteristic feature is the extremely low hygroscopic property (2–5 %). When boghead coals are extracted with a mixture of alcohol and benzene 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 of polyester type, having a linear-condensed structure and comprising interconnected relatively long methylene chains and rings. Because of the large number of hydroxyl and carbonyl groups in boghead coals, there are preconditions for the formation of hydrogen bonds. Furthermore, when evaluating the potential for using this material in hydrophobization processes, importance should be attached to the fact that its organic matter has relatively low thermal stability.

The research described here forms a basis for the development of new technologies for hydrophobisation of dispersed mineral materials using the products of deep chemical processing of peat. The studies allowed the development of scientific approaches to solve the problems of regulation and purposeful structural change of materials containing mineral binders and organic additives. At the same time the variety of composition and availability of the base raw material (peat) allows the production of construction materials with high hydrophobicity. The use of peat raw material for hydrophobization of construction materials partially solves the problems associated with traditional compositions, as a high degree of water repellency can be achieved in the modified materials with relatively low expenditure on the organic components.

## REFERENCES

- Afanasiev, I. (1941) A method for waterproofing of cement. Russian patent AS SSSR № 58128.
- Afanasiev, A. & Efremov, A. (2011) Effect of structuring on the density of the liquid in colloidal capillary porous bodies. *Theoretical Foundations of Chemical Engineering*, 45(1), 120–126.
- Afanasiev, A., Gamayunov, S. & Misnikov, O. (1999) Structurization Processes during drying of sapropels with varying ash content. *Colloid Journal*, 61(3), 274–279.
- Agde, G. & Lyncker, L. (1930) *Die Vorgänge bei der Stuckkoksbißung: Auf Grund experimenteller Untersuchungen (The Processes of Stucco Coking: Based on Experimental Investigations)*. Kohle-Koks-Tcer, Frankfurt am Main, 78 pp. (in German).
- Batrakov, V. (1998) *Modifitsirovannyie Betony. Teoriya i Praktika (Modified Concretes. Theory and Practice)*. Stroyizdat, Moscow, 560 pp. (in Russian).
- Bazhenov, D.A., Tarnovskaya, L.I. & Maslov, S.G. (1999) Fiziko-khimicheskie osnovnyi modelirovaniya reaktsiy termoliza torfa. Guminovyye i fulvokisloty kisloty (Physical and chemical bases of modelling of peat hydrolysis reactions. Humic and fulvic acids). *Khimiya Rastitelnogo Syrya (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», 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», Minsk, 168 pp. (in Russian).
- Bryuzgin, E., Klimov, V., Dvoret'skaya, O., Man', L., Navrotsky, A. & Novakov, I. (2014) Hydrophobization of cellulose-containing materials with fluoroacrylic polymers and fatty carboxylic acids. *Russian Journal of Applied Chemistry*, 87(8), 1119–1125.
- Butenko, A. & Luginina, I. (2004) Poluchenie gidrofobnogo tsementa pri vvedenii mestnoy dobavki - otkhoda maslozhировой promyshlennosti (Obtaining of hydrophobic cement with introduction of local additive - oil and fat industry wastes). *Tsement i ego Primenenie (Cement and its Use)*, 5, 65–66 (in Russian).
- Efimova, E. & Pukhova, O.V. (2013) Izmenenie vodno-fizicheskikh svoystv torfyanogo syrya pri mekhanicheskoy pererabotke i sushke. (Changes in the water-physical properties of peat raw material upon mechanical processing and drying). *Trudy Instorfa (Proceedings of Instorfa)*, 8(61), 44–47 (in Russian).
- Ferronskay, A. (2004) *Gipsovyie Materialy i Izdeliya (Proizvodstvo i Primenenie) (Gypsum Materials and Products (Production and Use))*. Izdatelstvo Assotsiatsii Stroitel'nykh Vuzov, Moscow, 488 pp. (in Russian).
- Gorchakov, G. & Bazhenov, Y. (2012) *Stroitel'nye Materialy (Construction Materials)*. Kniga po

- trebovaniyu, Moscow, 688 pp. (in Russian).
- Jung, V. (1949) O drevnerusskikh stroitelnykh rastvorakh (About old Russian mortars). In: Budnikov, P.P. (ed.) *Sbornik Nauchnykh Rabot po Vyazhushchim Materialam (Collection of Scientific Works on Binding Materials)*, Promstroyizdat, Moscow, 226–234 (in Russian).
- Khigerovich, M. (1957) *Gidrofobnyi Tsement i Gidrofobno-plastifitsiruyushchie Dobavki (Hydrophobic Cement and Hydrophobically Plasticizing Additives)*. Gosudarstvennoe izdatel'stvo literatury po stroitel'nyim materialam, Moscow, 208 pp. (in Russian).
- Khigerovich, M. & Baier, V. (1979) *Gidrofobno-Plastifitsiruyushchie Dobavki Dlya Tsementov, Rastvorov i Betonov (Hydrophobically-Plasticizing Additives for Cements, Mortars and Concretes)*. Stroyizdat, Moscow, 125 pp. (in Russian).
- Kosinov, E. (2012) Povyshenie neproniyaemosti tsementnogo kamnya pri vvedenii gidrofobiziruyushchikh dobavok na nositele (Increasing permeability of cement stone when introduced hydrophobizing additives on the carrier). *Tekhnologii Betonov (Concrete Technologies)*, 9-10(74–75), 57–59 (in Russian).
- Kunin, A. & Lapshin, D. (2015) Gidrofobizatsiya amorfnoho dioksida kremniya razlichnykh marok v protsesse mekhanokhimicheskogo modifitsirovaniya (Hydrophobization of amorphous silicon dioxide of different brands in process of mechanical chemical modification). *Izvestiya Vysshikh Uchebnykh Zavedeniy. Seriya: Khimiya i Khimicheskaya Tekhnologiya (Proceedings of Higher Educational Institutions. Series: Chemistry and Chemical Technology)*, 58(9), 38–42 (in Russian).
- Lishtvan, I., Falyushin, P., Kraiko, V. & Dudartchik V.M. (2012) Piroлиз burykh ugley Lelchitskogo mestorozhdeniya (Pyrolysis of Lelchitsky brown coal deposit). *Inzhenerno-fizicheskiy Zhurnal (Journal of Engineering Physics)*, 85(6), 1235–1241 (in Russian).
- Lishtvan, I. & Korol', N. (1975) *Osnovnye Svoystva Torfa i Metody ikh Opredeleniya (Basic Properties of Peat and Methods for their Determination)*. Izdatelstvo «Nauka i Tekhnika», 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», Minsk, 232 pp. (in Russian).
- Misnikov, O. (2006) Physicochemical principles of hydrophobization of mineral binders by additives produced from peat raw material. *Theoretical Foundations of Chemical Technology*, 40(4), 423–430, doi: 10.1134/S0040579506040130.
- 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, doi: 10.1134/S1995421214030149.
- Misnikov, O. & Chertkova, E. (2014) Hydrophobic modification of mineral binders by additives produced from peat. *Eurasian Mining*, 1(21), 63–68.
- Misnikov, O., Pukhova, O., Belugin, D. & Ashcheul'nikov, P. (2004) Hydrophobization of dry building mixtures by additives produced from organic biogenic materials. *Construction Materials*, 10, 2–4.
- Paschenko, A. (1987) *Polifunktsionalnyie Elementoorganicheskie Pokrytiya (Multi-functional Elementoorganic Coatings)*. Vishcha shkola, Kiev, 198 pp. (in Russian).
- Paschenko, A., Serbin V. & Starchevskaya, E. (1985) *Vyazhushchie Materialy (Binding Materials)*. Vishcha shkola, Kiev, 440 pp. (in Russian).
- Rakovskii, V. (1949) *Obshchaya Khimicheskaya Tekhnologiya Torfa (General Chemical Technology of Peat)*. Gosudartstvennoye energeticheskoye izdatelstvo, Moscow, 363 pp. (in Russian).
- Rakovskii, V., Kaganovich, F. & Novichkova, E. (1959) *Khimiya Pirogennykh Protsesov (Chemistry of Pyrogenic Processes)*. Izdatelstvo AN BSSR, Minsk, 208 pp. (in Russian).
- Sednev, V. & Savchenko, N. (2011) Kremniyorganicheskie kompozitsii dlya naneseniya zaschitnykh gidrofobiziruyushchikh pokrytiy na stroitelnyie materialy (Organosilicon compositions for application of protective hydrophobizing coatings onto construction materials). *Fizika i Khimiya Obrabotki Materialov (Physics and Chemistry of Materials Processing)*, 6, 76–81 (in Russian).
- Smol'yaninov, S. & Maslov, S. (1975) *Termobriketirovanie Torfa (Hot Briquetting of Peat)*. Izdatelstvo Tomskogo gosudartstvennogo universiteta, Tomsk, 108 pp. (in Russian).
- Sulman, M., Kosivtsov, Yu., Sulman, E., Alforyov, V., Lugovoy, Yu., Molchanov, V., Tyamina, I., Misnikov, O., Afanashev, 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.

- Taylor, H. (1996) *Khimiya Tsementa (Cement Chemistry)*. Mir, Moscow, 560 pp. (in Russian).  
Tomson, A. & Naumova, G. (2009) *Torf i Produkty ego Pererabotki (Peat and Products of its Processing)*. Belaruskaya navuka, Minsk, 328 pp. (in Russian).  
Volzhensky, A., Burov, Y. & Kolokolnikov, V. (1979) *Mineralnyie Vyazhuschie Veschestva (Mineral Binders)*. Stroyizdat, Moscow, 480 pp. (in Russian).
- Submitted 25 May 2016, revision 13 Sep 2016*  
*Editor: Olivia Bragg*
- 

Author for correspondence:

Dr Oleg Misnikov, Geotechnology and Peat Production Department, Tver State Technical University, Afanasiy Nikitin Emb. 22, Tver, Russia.

Tel: +7 4822 78 93 79 (office), +7 903 695 56 12 (mobile); E-Mail: oleg.misnikov@gmail.com