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EFFECT OF ACTIVATED TEMPERING WATER AND FILLING AGGREGATE SURFACE ON THE HARDENING KINETICS OF GYPSUM BLENDS

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Abstract.

The effect of microwave irradiation on the water structure has been studied; it was proven by the change in the electrical conductivity and viscosity of water. The hardening kinetics of gypsum slurry has been studied by measuring the electrical resistance. The dependence of the rate of change of the electric resistance has been examined in the process of hardening the hemihydrate gypsum. The change in the water properties during the water absorption of a certain amount of microwave energy was evaluated by its changed specific electric conductivity and viscosity coefficient, which were determined according to known methods. The hardening kinetics of gypsum tempered with activated water has been studied.

Different kinetic regularities of gypsum hardening on the water not treated and treated with microwave irradiation have been observed; such regularities were appropriately reflected in the physical and mechanical properties of gypsum samples. The optimal microwave treatment conditions have been selected to speed up the hardening process of gypsum. The nanostructures have been obtained, and their effect on hardening the gypsum and sand blends have been investigated. A method to produce nanosystems using thin films in aqueous solutions of various dispersed-substrate substances in an electromagnetic microwave field has been proposed. The effect of some nanosystems on the hardening kinetics of gypsum and sand compositions and their physico-mechanical characteristics have been studied. A significant increase in the strength of gypsum binder has been found.

Key words: microwave irradiation, activation, electrical resistance, hardening kinetics, specific electric conductivity, viscosity coefficient, binder.

Introduction. It is known that the properties of composite materials are highly dependent on the properties of the components in their composition [1]. Therefore, a change in the properties of the components of composite blends

Vyacheslav Ivanovich Pavlenko**et al.* /*International Journal of Pharmacy & Technology* can selectively modify the properties of the latter. The main components of blends of inorganic binders include a binder, a filling aggregate and tempering water [2].

Currently, different methods of changing the properties of the blending components, especially tempering water, are known [3]. Typically, these processes are called activation. In our view, there is a lack of attention on the studies related to the water activation by the microwave irradiation, and basic water treatment parameters remain unknown.

Main Part. This paper studies the effect of microwave irradiation of distilled water on the gypsum hardening kinetics and proposes a method for producing nanocoatings (nanolayers) of various substances, it also investigates the effect of these nanostructures on hardening the gypsum and sand blends and their physical and mechanical characteristics.

The hardening kinetics of gypsum slurry (water-gypsum ratio - 0.6) was studied by the method of electrical resistance [4] measured using the alternating current bridge E7-11.

The microwave irradiation of water was carried out in Samsung CE101R microwave oven with a frequency of 2.45 GHz and power of 900 W. For this purpose, a glass beaker with 0.25 l of distilled water was placed in an oven and exposed to microwave electromagnetic field of different energy.

The change in the water properties during the water absorption of a certain amount of microwave energy was evaluated by its changed specific electric conductivity and viscosity coefficient, which were determined according to known methods [5].

Physical and mechanical properties of the hardened gypsum samples were measured according to GOST 310.4-76; 10180-74.

Figure 1 shows the kinetic curves of the rate of change of the gypsum electric resistance when the gypsum is tempered with the distilled water nonirradiated (Curve 1) and irradiated (Curve 2,3,4) with microwave electromagnetic field. The figure (Curve 1) displays that initially this rate (section *ab*) does not change significantly, then a sharp increase to the maximum value (section *bc*) follows. Later, a rapid drop in electrical resistance rate (section *cd*) and then its slow decrease (section *df*) are observed. Earlier in the work [6], a similar dependence was obtained for the hardening rate of beta hemihydrate gypsum using differential scanning calorimetry.

A number of complex parallel processes takes place during gypsum hardening: dissolution, hydration, colloidation, crystallization and recrystallization of hardening products [7].

According to [8], when mixing gypsum and water hydration and hydroxylation of both dissolved and undissolved gypsum particles occur. The hardening process of gypsum binders are due to acid-base condensation of hydroxylated particle of these binders, which leads to their colloidation and crystallization.

The highlighted sections in Figure 1 reflect a predominant flow of various processes in the hardening gypsum composition.

A slight change in the electrical resistance rate on sections *ab* can be explained by the flow of competing processes of dissolution and condensation of hydroxylated gypsum particles.

A sharp increase in the rate of change of the electrical resistance from the time corresponding to point *b* can be explained by the prevalence of the process preventing any further increase in the concentration of dissolved particles.

It is obvious that such process can be represented by condensation process accompanied by the formation of colloidal particles.

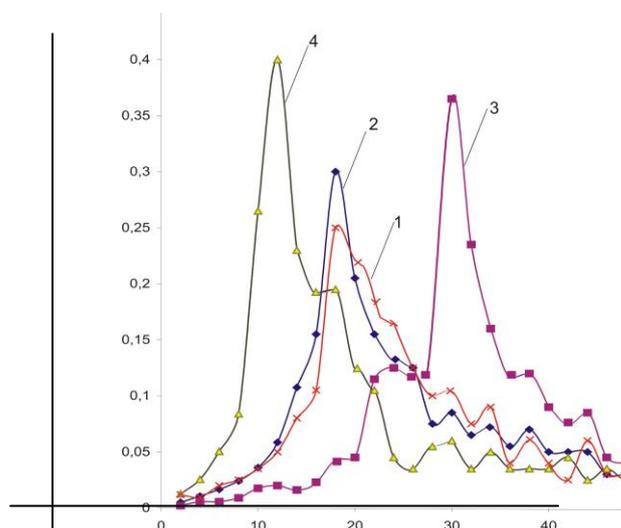


Figure 1. Dependence of the rate of change of the electric resistance in the process of hardening the hemihydrate gypsum (1- tempered with normal water; 2- tempered with water treated with absorbed energy microwaves of 0.9 kJ/mol; 3-1.1 kJ/mol; 4-1.4 kJ/mol)

Rapid reduction of the electrical resistance rate on section *cd* might be due to generation of a significant amount of water because of condensation and coagulation processes of the formed colloidal particles. The latter contributes to further hydroxylation of gypsum particles and thus decrease in the electrical resistance rate of the system.

The resulting slow drop in the rate of change of the electrical resistance on section *de* can be associated with the predominant formation of condensation and crystallization structures followed by their recrystallization impeding the motion of charged particles.

Comparison of curves in Figure 1 indicates that the above mentioned stages characterizing the predominant flow of relevant physical and chemical processes also take place in the case of using water irradiated with microwave field for the tempering process. However, depending on the amount of microwave energy absorbed with water the duration of these gypsum hardening processes is changed. For all kinetic curves reflecting the gypsum hardening in the water activated by microwave irradiation, an increase in the peak of curves is observed compared to the increased peak of curve obtained using nonirradiated water.

Thus, when tempering the gypsum with water treated with absorbed energy microwaves of 0.9 kJ/mol, any change in the kinetic curve is practically determined only by a peak value. By increasing the amount of microwave energy absorbed with water (Curve 3), there is an extension of the area (induction period) corresponding to section (ab) on Curve 1. The latter indicates a slowdown in the physical and chemical processes described by this stage. Primarily, this applies to the processes of hydration and hydroxylation. As a result, the flow of physical and chemical processes corresponding to stages bc, cd and de has also a time offset the right.

However, in this case the processes of colloidation, condensation and crystallization are more intensive. The peak of Curve 3 is higher than the peaks of Curve 1 and 2. With further increase in the amount of absorbed energy (Curve 4), the kinetic curve of gypsum hardening is considerably offset to the left; it indicates that there is a significant increase in the rate of physical and chemical processes corresponding to the above stages.

The observed different kinetic regularities of gypsum hardening on the water not treated and treated with microwave irradiation should be appropriately reflected in the physical and mechanical properties of gypsum samples (Table 1).

Comparison of the peaks with the physical and mechanical properties of gypsum samples indicates a correlation among them. Thus, any change in the physical and mechanical characteristics of the gypsum samples can be judged by the peaks of the kinetic curves of gypsum hardening.

Table 1. Physical properties of the water and physical and mechanical values of gypsum samples

Absorbed energy, kJ/mol	Compressive strength, MPa	Electrical conductivity, $10^3 \text{ ohm}^{-1} \text{ m}$	Viscosity coefficient, $\text{mPa} \cdot \text{s}$
0.0	4.0	0.900	1.000
0.9	5.6	0.943	0.954
1.1	5.8	0.952	0.940
1.4	6.7	1.070	0.928
2.7	5.5	0.970	0.966

Changing the duration and intensity of physical and chemical processes observed at gypsum hardening on the kinetic curves of the physical and mechanical properties of gypsum samples can be explained by a change in the properties of water treated with microwave irradiation.

Really, when treating water with microwave irradiation its properties such as electric conductivity and viscosity (Table 1) change. The table shows that with increasing the absorbed microwave energy the specific electric conductivity of water first increases and then decreases, however, the viscosity first decreases and then increases.

Many water properties are determined by the ability of its molecules to form associates with varying degrees of association due to the hydrogen bonds. In other words, the water is a monomer-polymer mixture. According to [9], about 30% of all water molecules exist in the form of individual molecules, 40% are part of the stabilized associates with a specific structure, they are called clusters, and 30% fall fo associates with a low degree of association (oligomers).

The electrostatic part of intermolecular interactions, which largely determines the orientation of interacting water molecules at an equilibrium distance, plays a decisive role in the formation of hydrogen bonds. This is due to the fact that a water molecule is a dipole with a high dipole moment. In this regard, it can be assumed that the effect of the electromagnetic field, first of all, its electrical component, on a change in the water structure is associated with a significant polarizability of its molecules and, therefore, it should greatly affect the processes, in which a self-dissociation of water occurs.

The formed hydrogen and hydroxyl ions can interact with the water polymers and charge them appropriately, whereby the concentration of counter ions increases in water, and thus, the medium reaction changes. The indicator method found a decrease in water pH after water treatment with microwave irradiation. The work [10] notes an increase in pH of magnetic water. In this connection, the authors of this article suggested a hypothesis of the formation of proton clusters $[nH_2O \cdot H^+]$ retaining a proton sufficiently well, which leads to an increase in the concentration of free hydroxyls. According to our experimental data, it can be assumed that in the water treated with microwave field hydroxyl clusters $[nH_2O \cdot OH]$ appera, and therefore the concentration of hydrated hydrogen ions H_3O^+ increases therein. An increase in the electrical conductivity of the water irradiated with microwave field and the water acidity can be explained by the appearance of charged clusters and free ions in the water.

It is obvious that the water viscosity will be determined by the movement of water layers comprising a polymeric form against each other. Identical charges of clusters as a result of electromagnetic water treatment gives rise to the

repulsive forces between them and thus to the lower internal resistance during their movement against each other. The nanolayers were formed out of $4.5 \cdot 10^{-6}$ m films of aqueous solutions on dispersed solid surface in electromagnetic microwave field.

The quartz sand with a specific surface area of $18.2 \text{ m}^2/\text{kg}$ was used as a dispersed substrate. The water films on the substrate were obtained by mixing intimately estimated amounts of quartz sand and aqueous solution of various substances and concentrations.

Then the resulting wet mass was subjected to microwave irradiation in Samsung CE101R microwave oven with a frequency of 2.45 GHz and power of 900 W. Heating with microwave irradiation is characterized by high rate and high efficiency.

This is caused by the fact that if microwaves have an impact on wet sand mass heating occurs simultaneously from inside throughout its volume due to the effect of dielectric losses. It is obvious that due to such impact the nanolayers of the same thickness should be formed on the quartz sand surface.

To obtain the nanolayers, solutions of a nitrogen containing cationic substance (cationic surface-active agent) and calcium sulphate were used. The thickness of the formed nanolayers on the quartz sand surface was evaluated by calculation using published data of the landing site's values.

The specific surface area of quartz sand was evaluated by a methylene blue (MB) monolayer capacity on the basis of its adsorption isotherms. In order to construct the latter the photometric method determined its amount in the solution before and after adsorption on the sands.

The hardening kinetics of the gypsum and sand blend 1:2 (gypsum of grade G-5, VG-0.8) was studied by the method of electrical resistance measured using the alternating current bridge E7-11.

The strength characteristics of the hardened gypsum and sand samples was determined after 24 hours of dry hardening on the cube-shaped samples, which side dimension made up $2.5 \cdot 10^{-2}$ m.

Figure 2 presents the kinetic curves of the rate of change of the electrical resistance during hardening the gypsum and sand samples with absent nanolayers (Curve 1) and nanolayers formed on the surface of sand of different thickness (Curve 2-4).

Figure 2 shows that the hardening process of the gypsum and sand blend is accompanied by a number of complex parallel processes: dissolution, hydration, colloidation, crystallization and recrystallization of hardening products.

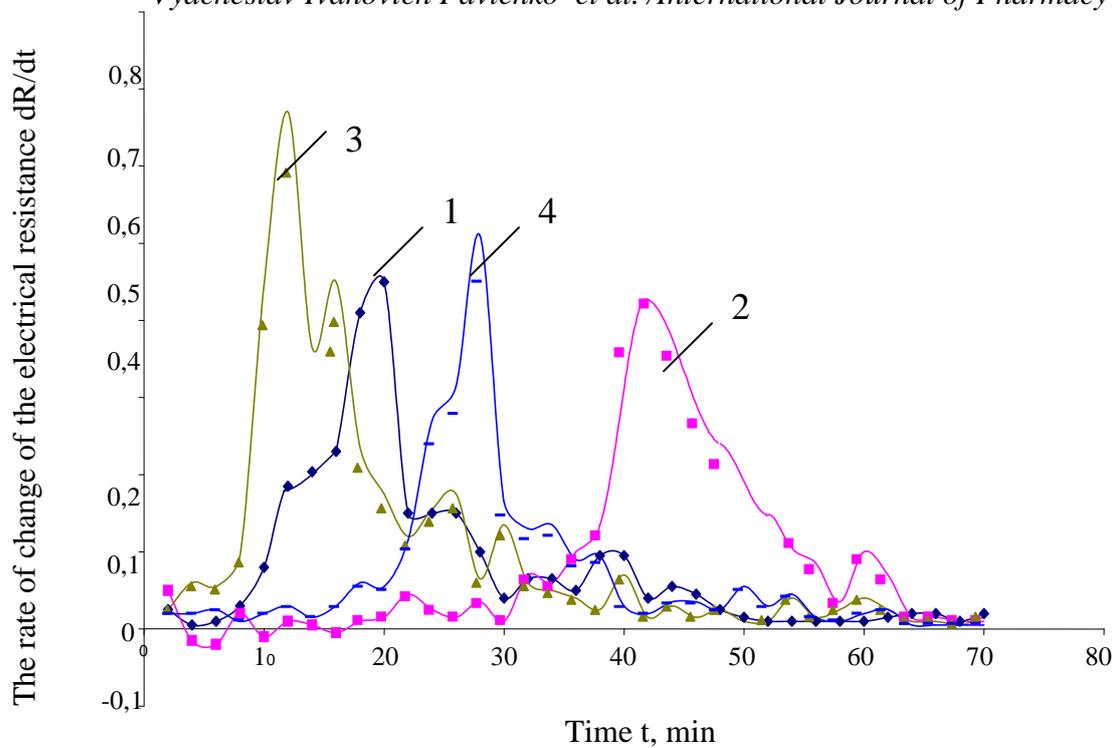


Figure 2. Dependence of the rate of change of the electric resistance in the process of hardening the gypsum and sand composition: 1 – with nanolayers absent on the sand surface; 2 – with 2–100 nm; 3–10 nm; 4–1 nm nanolayers of cationic surface-active agent formed on the sand surface

The highlighted areas in the figure (Curve 2) reflect a predominant flow of various processes in the hardening gypsum composition. Comparison of curves in the figure indicates that the above mentioned stages characterizing the predominant flow of relevant physical and chemical processes also take place in the case of using the sand with nanolayers applied on its surface. However, depending on the thickness of nanolayers the duration and intensity of the specified processes of hardening of the blend can be changed. Thus, during formation of a 100 nm nanolayer on the sand surface (Curve 2), there is a significant extension of the area (induction period) corresponding to section (ab) on Curve 1. The latter indicates a slowdown in the physical and chemical processes described by this stage. Primarily, this applies to the processes of hydration and hydroxylation. Slower hydroxylation and hydration processes can be explained by the formation of hydrophobic layers on the sand surface and a considerable shielding of the substrate. Upon reaching the desired concentration of hydrated and hydroxylated particles, the flow of physical and chemical processes corresponding to stages bc, cd and de becomes possible. The intensity of the flow of these processes and the processes described by Curve 1 is almost the same. Nevertheless, it can be assumed that the difference of induction periods in the considered cases should lead to the formation of other structures.

During the formation of a 10 nm surface layer on the sand substrate (Curve 3), there is a significant increase in the intensity of all physical and chemical processes that characterize the hardening process of the gypsum and sand

blend. The observed increase in the hardening rate of the considered composition can be attributed to the fact that the surface layers of the mentioned thickness have a large specific surface area, and therefore, they have high reactivity and apparently catalytic properties.

A 1 nm layer formed on the sand surface (Curve 4) just like a 100 nm layer formed on the sand substrate result in slower processes of dissolution, hydration and hydroxylation. However, the rate of these processes described by Curve 4, as well as that of the processes of colloidation and crystallization is noticeably higher than the rate of the processes described by Curve 2. This fact indicates that the nanolayer hydrophobicity and shielding of a sand substrate is considerably lower in this case.

Changed duration and intensity of physical and chemical processes responsible for the formation of gypsum and sand structures should, due to the presence of nanoscale layers (cationic surface-active agent) on the sand surface, also lead to corresponding changes in the physical and mechanical properties of hardened samples. In fact, Table 2, which shows the strength characteristics of samples with absent nanolayers and nanolayers of different thickness formed on the sand surface, presents that the strength of samples with the nanolayers applied on the sand surface is considerably larger compared with the control sample.

Table 2. Physical and mechanical testing of gypsum and sand samples.

Thickness of nanolayers on sand surface, nm	R _{compr} , MPa	Growth of strength, %
–	3.3	–
100	5.3	60
10	6.6	100
1	5.9	78

However, a certain correspondence of the peaks of kinetic curves (Figure 2) and the strength characteristics of samples is observed. Higher value of the peak of the kinetic curve also corresponds to the growth in strength of the samples. The increased strength of the samples with a filling aggregate, the surface of which has a 100 nm nanolayer, compared with a control sample at essentially the same intensity of the condensation and crystallization processes occurring therein is associated with the extension of induction period and the formation of apparently a more fine-grained structure in this the case. Figure 3 presents the kinetic curves of the rate of change of the electrical resistance

during hardening the gypsum and sand samples with absent nanolayers (Curve 1) and nanolayers formed on the sand surface with 100 nm nanolayers of calcium sulphate (Curve 2).

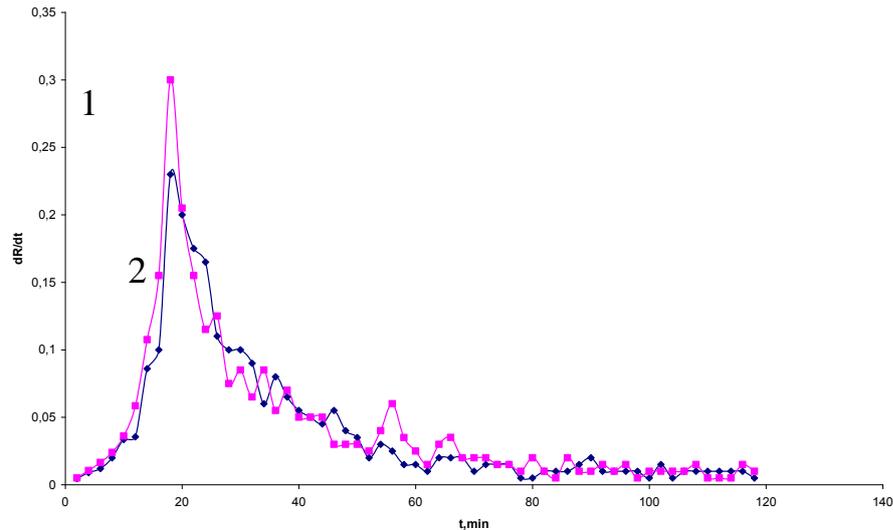


Figure 3. Dependence of the rate of change of the electric resistance in the process of hardening the gypsum and sand composition: 1 – with nanolayers absent on the sand surface; 2 – with nanolayers formed on the sand surface with 100 nm nanolayers of calcium sulphate.

Figure 3 shows that the duration of the physical and chemical processes that result in the formation of gypsum and sand structures is the same in both cases. However, the intensity of coagulation, condensation and crystallization processes is significantly higher when calcium sulphate nanolayers are present on the sand surface; it indicates the catalyst activity of the nanolayers formed in this case. Increased intensity of the indicated processes should lead to an increase in strength of the samples. Indeed, the growth of their strength was 65% compared to the control sample.

Summary. Treatment of water with low-energy microwave electromagnetic field contributes to its significant activation, which manifests as a change in the water properties, physical and chemical processes of gypsum hardening and, eventually, a significant increase in the physical and mechanical characteristics of the gypsum samples. The nanolayers of considered substances present on the surface of a quartz filling aggregate result in a change of physical and chemical processes of hardening the gypsum and sand blends and formation of solid structures therefrom.

Conclusions. The effect of microwave irradiation on the water structure has been studied; it was proven by the change in the electrical conductivity and viscosity of water.

1. The hardening kinetics of gypsum tempered with activated water has been studied.
2. The optimal microwave treatment conditions have been selected to speed up the hardening process of gypsum; microwave energy absorbed with water - 2.7 kJ.

3. A significant increase in the strength of gypsum binder has been found. The increase in the bending strength was 20%, compressive strength - 67%.

4. The increased strength of the samples with a filling aggregate amounted to 65%.

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