Artificial aging of gypsum binder in terms of thermodynamics

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Abstract. Aging – is the process of improvement and stabilization of plaster binder properties. The effect of the process is determined by its conditions - the duration and relative humidity of the environment. It has been detected that a reduction of a specific surface area of plaster binder occurs by aging. This is related to the formation of nuclei of calcium sulfate dihydrate on the surface of the initial binding material. As a result of aging, the strength properties of gypsum stone have increased. The largest increase occurs in 3 days of aging at the relative humidity of 80%. The studied thermodynamic analysis of the process has showed that the most significant change of the primary structure of gypsum stone occurs under the conditions of aging. By the hardening of the binding material it leads to the formation a of thermodynamically stable and ordered structure of the artificial stone.

1. Introduction
At the present time field of plaster binders application is expanding due to the growing scale of the introduction of advanced technologies which provide the reduction of fuel-energy and material resources. It is especially important to have stability of the quality of gypsum binders in order not to break the technological mode of production of materials and products based on them.

2. Relevance, problem statement
One of the most effective ways of improvement and stabilization of properties – is an artificial aging of plaster binders. The essence of this process is in the partial hydration of the binding materials by storage them at different relative air humidity. Improvement and stabilization of the properties of gypsum binders is achieved only by storage of material under certain conditions within the required period.

3. Theoretical part
The material used for research is gypsum binder of β-modification of G4 grade; it has been selected from the kettle after cooking process.

The aging of gypsum binder was carried out during storage at temperature of 20°C and relative humidity of 60%, 80% and 100% (φ = 0.6; 0.8; 1.0) within 14 days, because the greatest interest for gypsum binder manufacturers is the early stages of the aging in order not to prolong the overall production cycle.

Thermodynamic characteristics of the process of hardening of gypsum binder after storage under various conditions (the rate of the hydrate formation, the degree of completeness of hydrate formation,
the degree of completeness of structure formation, the entropy production during hardening) were
determined on the basis of experimental data obtained by potentiometric method [1,2].

Adsorption of water vapor on the surface of the original hemihydrate plaster particles and the
formation of liquid films occurs under the influence of humid air. Under conditions of high relative
humidity ($\varphi = 1$) the condensation of water vapor with the formation of film liquid of 90 micron
thickness, which almost does not change during the process of aging take place. This indicates that
water in the film has liquid-drop state (volumetric water).

At the same time, when $\varphi = 0.8$ values of film thickness are in the range of 5.6...8.1 microns, when
$\varphi = 0.6 \approx 3$ microns. The water in the film $\delta \approx 8 \mu$m differs in properties from the liquid film $\delta \approx 90$
$\mu$m, and this may lead to a change in the mechanism of hydration of plaster binder by its aging [3].

According to [4], the water films which are formed on the surface of gypsum particles when
$\varphi \leq 0.8$ have high strength $\approx 25$ MPa which is comparable to the strength of a solid. Consequently, the
moisture in this liquid film probably will not be able to ensure the development of the process of
hydration of the original hemihydrate plaster by trough solution mechanism.

When $\varphi \geq 0.8$ condensation of water vapor is preferable in the place of high activity of particles
(surface and internal defects), as well as in ultrathin pores (cracks). In such conditions there is the
hydration of hemihydrate plaster and its conversion to calcium sulfate dihydrate [5, 6].

Thus there is an enlargement of particles and self-healing of defects of the crystal structure (figure
1). It must be assumed that, depending on the conditions of hydration (by different thickness of liquid
film) crystals of dihydrate of different morphology and size occur, as well as formation of
modifications of calcium sulfate hydrate with different content of crystallization water is possible.

![Figure 1. Formation of dehydrate during the aging [5].](image)

Exactly these two phenomena explain the stabilization of the technological properties of plaster
binders and determine the process of aging. The formed crystals of calcium sulfate dehydrate are
centers of crystallization, therefore, they influence on the nature of hardening of plaster binder and
participate in the formation of the structure of plaster stone [3].

4. Results of experimental studies
As follows from the experimental data presented in table 1, the conditions of aging influence on the
strength properties of gypsum stone, and the maximum strength is reached in three days of aging at a
relative air humidity equal 0.8.

| Air humidity | Compressive strength, MPa |
|--------------|---------------------------|
|              | without aging 3 days 7 days 14 days |
| $\varphi = 0.6$ | 4.72 4.83 4.41 |
| $\varphi = 0.8$ | 4.1 5.07 4.64 4.37 |
| $\varphi = 1.0$ | 4.59 4.51 4.2 |
For the explanation of this result we shall consider the change of kinetic and thermodynamic characteristics of the process of hardening of plaster binder which is subjected to aging in more detail.

Figure 2 illustrates the kinetics of hydration of the plaster binder that has been subjected to aging under different conditions. As follows from the obtained data, a binder aged by $\phi = 1$ has a highest rate of hydration, and with the increase of duration of aging the rate of hydration grows also. This is due to the increase of formation of calcium sulfate dihydrate produced under present conditions of aging, which in the subsequent hydration of plaster binder leads to the increase of the degree of supersaturation and, consequently, to the acceleration of the hydration process [5]. The increase of the rate of hydration should be noted by growth of the duration of the aging and under other different conditions [8].

Analysis of changes of the thermodynamic coordinates of hardening process (degree of completeness of hydrate and structure formation) has shown that the highest rates are achieved during hardening of binding material subjected to aging for 3 days at a relative humidity $\phi = 0.8$ (Figure 3 and 4).
Thus, the increase of aging duration by more than 3 days does not lead to significant increase of the degree of completeness of hydrate structure formation, as well as the strength of gypsum stone. The growth of these values in the process of aging during 3 days is caused by the convergence of particles to the required distance for the coalescence of individual particles of a disperse system [9,10]. This can be achieved through the formation of "nucleus-bridges" between particles of calcium sulfate dihydrate. It should be noted that, according to [9,11], the occurrence of nuclei of crystallization – is energy unfavorable process, but it is substantially facilitated in the presence of interphase boundaries, particularly if the substrate material is close to a new phase by its crystallochemical parameters. The role of the substrate is performed by the crystals of calcium sulfate dihydrate which are formed in the process of aging. With a high degree of supersaturation (at the beginning of hydration) formation of nuclei is energy favorable, and by the reduction of the degree of supersaturation the growth of forming crystals becomes preferable. Since the hardening of gypsum binder subjected to aging at \( \phi \leq 0.8 \), the fewer degrees of supersaturation occurs. So, in this case the crystal growth is predominant, that is conditional on a high degree of completeness of structure formation, i.e there are the conditions for formation of the optimal final structure of gypsum stone.

![Figure 5. Microstructure of gypsum stone after aging [12,13].](image1)

![Figure 6. The entropy production during hardening of gypsum binder.](image2)

The evaluation of the thermodynamic stability of the formed structure of gypsum stone has shown that structure with the maximum thermodynamic stability is formed of binder subjected to aging at \( \phi = 0.8 \) for 3 days (Figure 5), which is indicated by the minimum value of a quantity of entropy production in the binding system (Figure 6) [2]. Such a structure is characterized by a high degree of order and, consequently, a high strength of a stone (Table 1).
5. Conclusion

Thus, the performed thermodynamic analysis allows us to conclude that for improvement and stabilization of the properties of gypsum binders it is advisable to carry out artificial aging, when $\varphi = 0.8$ the duration should not exceed 3 days, because longer storage is not reasonable.

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