

The Role of pH Medium in Forming Binding Substances on the Base of Calcium Sulphate

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Abstract: Using the potentiometric method, which allows identifying all the existence domains of all forms of calcium sulphate, there was researched raw gypsum of various genesis and the products of its heat treatment. In this research there were used the rock gypsums of Baskunchakskoye, Dubinovskoye, Shedokskoye and Novomoskovskoye deposits, as well as synthetic gypsum c.p. and citrogypsum – a by-product of citric acid production. It was determined, that depending on the preponderance of sorption sites of acidic or alkaline nature, the products of gypsum heat treatment can be divided into the two groups. The first group is presented by gypsum products received by heating at 100...500°C, with predominantly electron-accepting properties of the surface. The second group is presented by gypsum products received by heating at 500...1100°C, with predominantly electron-donor properties. It is shown, that the ratio of acid-base sites in the products of heating synthetic and natural gypsums is different, especially in the temperature range 200...500 °C. There are derived relations, characterizing the influence of gauging fluid pH value on the solubility of calcium sulphate of various geneses, which allows forecasting the hydration kinetics of gypsum binders and their physical and mechanical properties.

Key words: Gypsum • Anhydrite • Genesis of rock gypsum • Products of gypsum heat treatment • pH • potentiometric method • Hydration kinetics • Hydrolysis

INTRODUCTION

The untreated rock gypsum shows neither acidic, nor alkaline properties. The reason is that each calcium ion is surrounded by six oxygen atoms, belonging to SO_4^{2-} groups and two oxygen atoms, belonging to the two molecules of water. Each molecule of water binds a calcium ion both with oxygen from this double layer and with oxygen from the neighboring layer. As a result there is formed a stable crystalline hydrate of calcium sulphate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

The binding energy of water molecules with these sites is various. So, any process, inducing deformation of the crystal lattice: heating, pressing or radiating, can activate the neutral salt. These products form an entirely new class of medium strength solid acids and show a specific activity and selectivity in a number of processes.

The acid-alkali properties of the original rock gypsum and products of its heat treatment, the behavior of gypsum binders at hydration have been studied by: Tanabe K., Altykis M.G., Fischer H.-B., Matveeva T.M., Ottemann J. etc.

According to Tanabe K. [1] the maximum acidity of the surface of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is achieved at the calcination temperature 230°C.

Altykis M.G. [2] has determined a relation of the water extract pH and the calcining temperature of gypsum from Kamsko-Ustinskoye deposit, having the maximum acidity in the interval of 250...350°C. He has made an assumption, that the activators of hardening of gypsum binders, containing semihydrate of calcium sulfate ($\beta\text{-CaSO}_4 \cdot 0,5\text{H}_2\text{O}$) and soluble anhydrite ($\beta\text{-CaSO}_4$ III) can be additives, possessing acid properties and the activators of hardening of gypsum binders, containing the insoluble anhydrite (CaSO_4 II) can be alkaline additives.

The influence of pH medium on CaSO_4 II hydration has been also researched by Fischer H.-B., Ottemann J., Israel D [3-6]. Matveeva T.M. [7] has studied the influence of pH medium on binding properties of phosphosemihydrate. The potentiometric research of raw gypsum of various genesis and products of its thermal processing has been for many years carried out at the inorganic chemistry department at BSTU named after V.G. Shukhov [8-10].

In spite of extensive research, carried out both by Russian and foreign scientists, there is still no integral theory, taking into account the influence of pH medium at all stages of obtaining gypsum building materials. The relevance of this research is determined also by the expansion of composite and multiphased dry gypsum mixes market, the development of which requires taking into account a number of criteria, including the value of pH medium.

The purpose of the work is finding out the role of pH medium at the main stages of producing gypsum binders and determining the optimum values of pH for hydration and hardening of calcium sulfate, which allows getting the efficient building materials on their base.

Materials and Methods of Research: As the original stock there were used rock gypsums of Baskunchakskoye, Dubinovskoye, Shedokskoye and Novomoskovskoye deposits, as well as synthetic gypsum c.p. and citrogypsum – a by-product of citric acid production. The presented gypsum raw stuff belongs to different genetic types and was selected with regard to its structure, texture, size of gypsum crystals and amount of admixtures. So, the amount of carbonates is the highest in the gypsum of Dubinovskoye deposit (7,7%) and citrogypsum from dumps (6,49%), is lower in the gypsum of Shedokskoye deposit (2,0%) and is the lowest (0,55%), in the gypsum of Baskunchakskoye deposit [8]. The rock gypsum of Shedokskoye deposit has the fine-mosaic oriented structure and the gypsum of Baskunchakskoye deposit – the average-mosaic oriented structure.

The natural raw gypsum has been initially ground until it fits through the sieve with mesh size 0,315 mm. The high-temperature modifications of calcium sulphate have been obtained by calcinating gypsum in ceramic cups in a muffle furnace and low-temperature modifications - by the isothermal treatment of gypsum in a drying box. In all experiments the mass of gypsum samples was permanent. The temperature control was performed in the bulk of material with a mercury thermometer up to 200 °C and with a thermocouple at

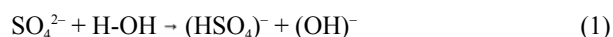
temperature above 300 °C. To determine pH and pCa there were used a pH-meter, millivoltmeter pH-121 and ion meter EV-74. As measuring electrodes there were chosen: calcium selective membrane electrode EM-Ca-01 and glass electrode ESL-63-07. The suspensions of binders ($B/T=12,5$) were prepared on boiled distilled water with $\text{pH}=7$. The composition was additionally activated with grinding it in a vibromill. The phase composition of calcium sulphate was controlled with X-ray phase analysis and by methodology, developed by B.S. Bobrov. To create acid medium H_2SO_4 was added into gypsum suspensions and to create alkaline medium NH_4OH was added.

The Main Part: At the initial stage of research by potentiometric method, which allows identifying the existence domains of the main forms of calcium sulphate [8, 9], there were researched the heat treatment products of raw gypsum of various genesis. There was derived a dependence of calcium sulphate suspensions' pH value from the temperature of gypsum heat treatment, which allows forecasting their catalytic activity. The lows at the acidity curves correspond to the ranges of the calcium sulphate's maximum activity and the peaks characterize the ranges of stable existence of this or that form of it. The absolute value of calcium sulphate suspensions pH depends on the gypsum genesis, the nature and quantity of admixtures, heat treatment conditions.

It is determined [8], that depending on the preponderance of sorption sites of acidic or alkaline nature, the products of gypsum heat treatment can be divided into the two groups. The first group is presented by gypsum products received by heating at 100...500°C, with predominantly electron-accepting properties of the surface. The second group is presented by gypsum products received by heating at 500...1100°C, with predominantly electron-donor properties. That the ratio of acid - alkali sites in the products of heating synthetic and natural gypsums is different, especially in the temperature range 200...500°C.

On contact with water the products of gypsum heat treatment polarize the water molecules in different ways, changing the acidity of the medium. We can single out two types of water molecules polarization. If water molecules are polarized by unoccupied orbitals of Ca^{+2} ions, the binder suspension is acidified. If water molecules are polarized by SO_4^{2-} ions the binder suspension takes on alkaline properties.

The stable phases of calcium sulphate polarize water due to lone-electron pairs of SO_4^{2-} groups, with H^+ ions departure by the scheme:



The active phases of calcium sulphate polarize water due to unoccupied orbitals of Ca^{+2} ions, with OH^- ions departure by the scheme:



In the first case the concentration of SO_4^{2-} ions and in the second case the concentration of Ca^{+2} ions in the suspension is reduced, by forming weak electrolytes. So, activators, which are electron pair donors, must contain the excess of SO_4^{2-} ions and alkaline medium and activators, which are electron pair acceptors, must contain the excess of Ca^{+2} ions and acid medium.

So, the dehydrated solid gypsum particles have amphoteric properties and, depending on the nature of surrounding particles, can enter into a reaction both with substances, exerting acidic properties and with substances, exerting alkaline properties. For which reason, the activators of calcium sulphate hardening can be represented by both acidic and alkaline admixtures, which can change the chemical equilibrium of reactions 1 and 2.

The next stage of the research was studying the solubility of gypsums of various geneses. The solubility of gypsum is accessed by pCa value of its suspensions. As a result of the research (Fig. 1–3) it was determined, that solubility of calcium sulphate crystalline hydrate depends on the pH value of gauging fluid, content of admixtures and genesis of raw gypsum. Artificial gypsums are more soluble, than the natural ones. The pH interval of gypsum suspensions with minimum solubility depends on the raw gypsum genesis. For the synthetic gypsum c.p. the pH interval = 5,5–5,7; for the natural gypsum of Baskunchakskoye deposit – 4,0–5,5; for the gypsum of Dubinovskoye deposit – 2,0–3,5; for the gypsum of Shedokskoye deposit – 3,5–4,5; for citrogypsum – 4,0–6,0.

For natural gypsum the curve part of pH with the maximum pCa value is wider and located in the more acidic range, due to the influence of carbonate admixtures. Disintegrating in the acidic medium, carbonates raise the pH value of gypsum suspensions, changing the solubility of calcium sulphate. This results in generating carbon dioxide, which contributes to forming the more porous structure of the material.

At pH = 3,5–7,5 the calcium sulphate suspensions have the maximum pCa value, which leads to their quick saturation with Ca^{2+} and SO_4^{2-} ions and gypsum crystallization. At $6,0 < \text{pH} < 4,0$ the pCa value of all types of gypsum increases. At that, in the alkaline medium the influence of raw gypsum genesis is smoothing and in the acid medium, it is, on the contrary, strengthened (Fig. 1).

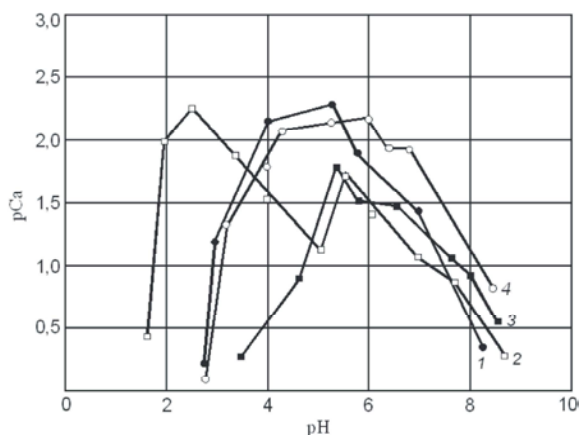


Fig. 1: The alteration of pCa of gypsum of various genesis depending on the gauging fluid pH value at the initial point of hydration:

- 1 - natural gypsum of Baskunchakskoye deposit;
- 2 - natural gypsum of Dubinovskoye deposit; 3 - synthetic gypsum c.p.;
- 4 - citrogypsum.

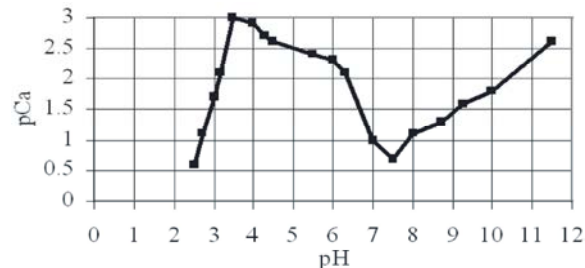


Fig. 2: The alteration of pCa of Shedokskoye deposit gypsum depending on the gauging fluid pH value.

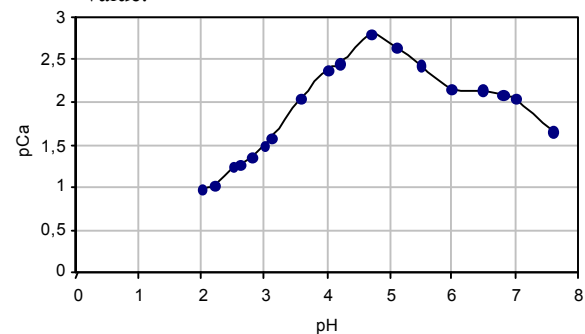


Fig. 3: The alteration of pCa of CaSO_4 II suspensions depending on the gauging fluid pH value.

Using the example of Shedokskoye deposit gypsum it has been determined, that in the alkaline medium at $\text{pH} > 8$ the pCa of gypsum increases (Fig. 3). The maximum solubility of gypsum is observed at $\text{pH} = 7-8$. The higher or lower values of pH increase the pCa value. The solubility of natural gypsum at $\text{pH} = 10,0$ is the same, as the solubility of artificial gypsum at $\text{pH} = 5,5$ and it is minimal.

The dependence of pCa of CaSO₄II, received by heating synthetic gypsum c.p, on the pH value of gauging fluid, is of the extremum character (Fig. 3). It is plotted on the base of data about pCa value of CaSO₄II in the solutions of salts and sulphuric acid and resembles the corresponding dependence for gypsum (Fig. 1, 2). It follows from the received data, that the pCa of anhydrite in suspensions with pH 2,0–3,5 is lower than the pCa of gypsum in water. By contrast to this, for suspensions with 3,5 < pH < 7,0 the pCa of anhydrite is higher than the pCa of gypsum. In the interval pH = 4,0–5,5 it is higher than the pCa of anhydrite in water; pCa of gypsum = 2,1; pCa of anhydrite = 2,7.

At designing gypsum binders it is essential to know not only the pH of their suspensions, but also how it alters in time. In this regard there was carried out the kinetic research of hydration of different phases of calcium sulphate.

The hydration and hydrolysis kinetic curves of natural and artificial gypsums' heat treatment products are identical in their shape and differ slightly by the absolute value of pH (Fig. 4-7).

Depending on their shape they can be divided into several groups (Fig. 4).

The first group is comprised of curves of gypsum heat treatment products in the range 100...355°C. They are characterized by having peaks and lows and rising of pH from weak-acid and neutral to weak-alkali.

The second group is comprised of curves of gypsum heat treatment products in the range 500...550°C. For these curves the pH value transits from weak-alkali to neutral.

We should especially single out the gypsum products of heat treatment at 450 °C, for which the kinetic curve almost doesn't alter and stays in the range of pH = 7. Products with such a shape of kinetic curve are formed at temperature > 360 °C. This is the temperature of the soluble anhydrite transition (β-CaSO₄ III) into CaSO₄ II. This corresponds to the exo-effect at DTA curve.

The third group is comprised of curves of gypsum heat treatment products at temperature > 600°C. These curves slightly alter in course of time and stay within the alkaline range of pH.

The hydration and hydrolysis kinetic curves of Shedokskoye deposit rock gypsum heat treatment products (Fig. 5) have the similar shape, which allows applying them for the raw gypsums of the other deposits.

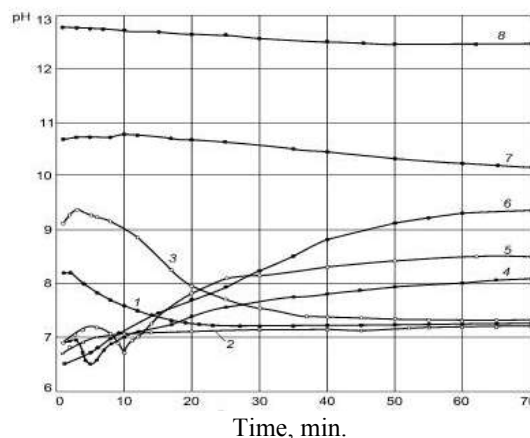


Fig. 4: The alteration of pH value of heat treatment products suspensions of Baskunchakskoye deposit gypsum: temperature of heating, °C: 1 - 500; 2 - 450; 3 - 550; 4 - 146; 5 - 149; 6 - 355; 7 - 600; 8 - 900.

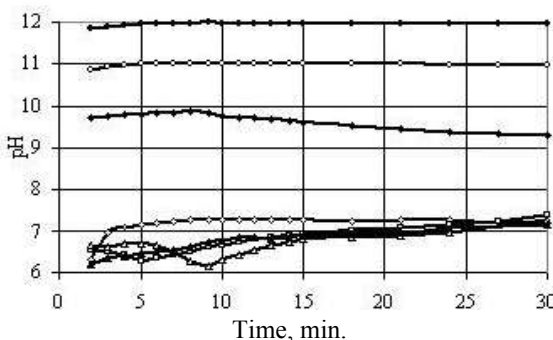


Fig. 5: The alteration of pH value of suspensions of various forms of calcium sulphate, received by heat treatment of Shedokskoye deposit raw gypsum at temperature, °C: 1 - 120; 2 - 130; 3 - 190; 4 - 500; 5 - 600; 6 - 700; 7 - 900.

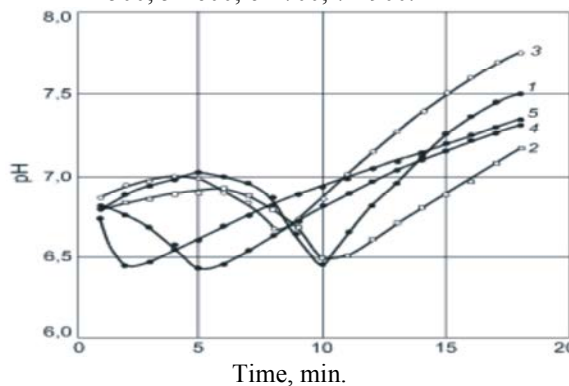


Fig. 6: The alteration of pH value of suspensions of heat treatment products of gypsum with different quantity of residual hydrate water, mas. %: 1 - 0,323; 2 - 2,27; 3 - 3,74; 4 - 6,52; 5 - 11,61.

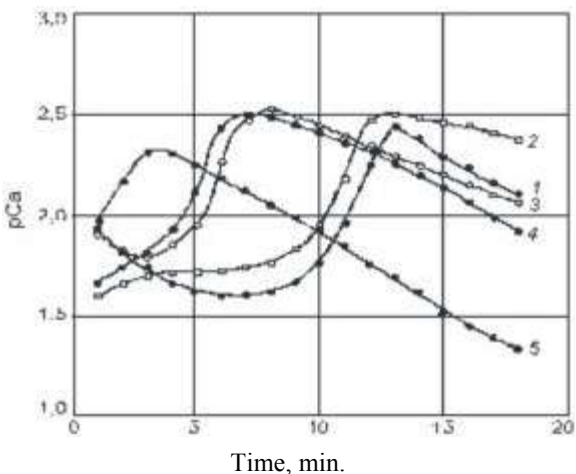


Fig. 7: The alteration of pCa value of suspensions of heat treatment products of gypsum with different quantity of residual hydrate water, mas.%:
1 - 0,323; 2 - 2,27; 3 - 3,74; 4 - 6,52; 5 - 11,61.

As it follows from the results of kinetic research, in the process of hydration the natural gypsums products of heat treatment at 100...355°C independently of their genesis change the sign of the surface from + to – and the gypsum products of heat treatment at 500...550 °C - from – to +. The gypsum, heated at temperature over 600 °C, on interaction with water slightly changes the charge of the surface. The most intensive forming of crystalline defects in gypsum is observed at 350...362 °C (positively charged sites) and 650...700 °C (negatively charged sites).

The shape of kinetic curves depends on the composition of calcium sulphate, the mixing water activity and presence of admixtures in gypsum. At the initial value $10,0 < \text{pH} < 5,0$ the effects at potentiometric curves are smoothed. The most informative are kinetic curves at the pH value of gypsum suspensions 6,0–7,0 (Fig. 6).

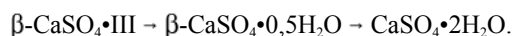
The character of pCa alteration at the initial period of hardening also depends on calcium sulphate composition, which is determined by the temperature and duration of gypsum heat treatment and the quantity of residual hydrate water.

Irrespectively of the nature of raw gypsum, in kinetic curves there can be singled out three sections, connected with certain periods of the calcium sulphate hydration and hydrolysis. The initial period in kinetic curves is connected with solution and hydrolysis of calcium sulphate. At that the pH value rises (fig. 6) and the pCa value lowers (Fig. 7). The hydrolysis of $\beta\text{-CaSO}_4 \cdot 0,5\text{H}_2\text{O}$

goes on by the mechanism of chemisorption by active sites of H^+ ions with disengagement of $\hat{\text{H}}^-$ ions into the solution. On the surface of gypsum building plaster the negatively charged active sites are prevalent. Acid salts increase the solubility of gypsum. In kinetic curves it is connected with lowering of pCa and increasing of Ca^{2+} ions concentration in the solution. These processes go on at the initial period of gypsum hydration.

Then there is observed the reduction of $\hat{\text{H}}^-$ ions concentration and acidifying of solution. The value of pCa goes up; the primary gypsum is formed. When the gypsum hydration process is over, the concentration of Ca^{2+} ions begins increasing again and the concentration of H^+ ions lowers. There occurs the recrystallization of the primary gypsum, which results in a slight weakening of gypsies materials.

It has been pointed out, that pCa kinetic curves can have one or two peaks. Two peaks are peculiar to the products of gypsum heat treatment at 180...190°C. Apparently, it's connected with two-stage hydration of $\beta\text{-CaSO}_4 \cdot \text{III}$, forming in this temperature range, according to the scheme:



The location of the peaks depends on the nature and activity of salts. In the presence of some admixtures $\text{CaSO}_4 \cdot \text{II}$ can be hydrated without intermediate stages straight to the dehydrate salt.

The kinetic research of hydration of different forms of calcium sulphate, carried out by applying both calcium selective membrane electrode and glass electrode, prove the various mechanisms of their hydration. The hydration of $\beta\text{-CaSO}_4 \cdot 0,5\text{H}_2\text{O}$, especially in the presence of gypsum, is quick and usually solidphase, by “crystal for crystal” replacing type, due to water molecules diffusion between the calcium sulphate layers, without any substantial transfer of matter from the dissolving semihydrate of calcium sulfate to gypsum. The pCa value of these suspensions lowers from the first minutes of hydration (Fig. 7). At this the section of pCa maximum value is extended considerably. The possibility of $\beta\text{-CaSO}_4 \cdot 0,5\text{H}_2\text{O}$ solidphase hydration mechanism can be explained by the similarity of its structure to the structure of gypsum. This mechanism is impossible for anhydrite due to significant difference between $\text{CaSO}_4 \cdot \text{II}$ and gypsum crystalline structures (isle structure for anhydrite and layer structure for gypsum correspondingly).

β -CaSO₄•III, CaSO₄•II and β -dehydrated semihydrate of calcium sulfate are hydrated through the solution. The pCa value for them initially lowers and the solution is saturated with Ca⁺² ions. The calcium sulfate is hydrated. Then the pCa rises and after achieving the maximum value begins to lower monotonely.

The presence of admixtures in the raw gypsum material results in altering of the hydrated systems' pH and affects the process of their hardening, which in its turn influences the physical and mechanical properties of the materials based on them. This is confirmed at studying citrogypsum-based binders and binders gauged with hard water. In the first case protons are involved into the reaction of citric acid forming from calcium citrate and in the second case – into the reaction of calcium and magnesium hydrocarbonates destruction.

The research, carried out on various gypsum binders, shows that mechanical strength depends on the activity of gauging water, temperature regime of receiving binders, quantity of hydrate water. This relation has the pronounced extremums. In the acidic medium the optimum pH of gauging fluid is 4,0-6,0 and in the alkaline medium - 9,0-10,0. The sharp drop of strength is observed at the gauging water's pH below 3. The strength of binders, gauged with acid solutions is higher, than the strength of binders, gauged with alkaline solutions.

CONCLUSION

- Suspensions of gypsum heat treatment products have different pH value, which depends on the gypsum genesis, temperature and time of heat treatment, the nature and quantity of admixtures.
- The high-temperature modifications of calcium sulphate (>650°C) have the alkaline medium and the low-temperature ones (<350°C) – weak-acid or neutral medium. Besides, the low-temperature phases of artificial gypsums have more acidic medium, than natural gypsums and the high-temperature phases, on the contrary, more alkaline medium. The water suspensions of anhydrite, received by heat processing of rock gypsums, have pH=11,8-12,2 and for artificial gypsum it is neutral.
- The pH value of gypsum heat treatment products suspensions is not permanent and alters due to processes, going on at the calcium sulphate hydration and structure formation.

- The processes, going on at hydration and hardening of gypsum binders, are vividly and informatively represented by kinetic curves of pH and pCa alteration. The shape of pH and pCa alteration kinetic curves depends on the calcium sulphate phase composition, which is determined by the temperature and duration of gypsum heat treatment and the quantity of residual hydrate water. Different phases of calcium sulphate have different shape of pH and pCa kinetic curves.
- On the base of the received data there is suggested a potentiometric method of controlling the binding materials' hydration and hardening processes; this method is based on studying the pH and pCa of hardening gypsum systems alteration kinetics.

Conclusions: So, the pH value of calcium sulphate suspensions is an essential parameter, which must be taken into account at all stages of designing and receiving gypsum binders. The acidic and alkaline mediums influence the gypsum heat treatment products in different ways and in each case there are their own optimal values of gauging fluid pH.

The most optimal are hydration conditions, at which at the initial period of hydration the pH is in the weak-acid range (pH = 5,5–5,7), which transits then to neutral. If the pH value of the hydrated binder in the initial period is below 4,0, this material doesn't achieve the neutral medium even at the last stages of hardening and is of low strength.

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