

# Structure formation of gypsum binder with zinc hydrosilicates

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**Abstract.** Due to high danger of mold fungi spores for humans, it is necessary to develop new fungicidal building materials, especially – materials that help to maintain biosafety in interior rooms. One of such materials is the fungicidal gypsum binder. The aim of the present work was to study the process of structure formation of gypsum in case of the presence of a previously developed fungicidal modifier which is based on hydrosilicate systems with zinc in different quantities. The studies were carried out in accordance with current regulations. The rheological and mechanical properties, including normal density, setting time and compressive strength were determined. The titrimetric method of analysis was used for determination of the content of calcium ions in the solution. It was revealed that the zinc content in the modifier does not affect the mobility of the mixture; however, it changes the rate of formation of the gypsum stone and also affects its strength. In particular, when the ratio  $v(\text{Zn})/v(\text{Si})$  is equal to 0.9, there was an increase of setting time. The mechanism of the formation of gypsum stone also changes: influence of both constructive and destructive factors simultaneously decreases. The latter was confirmed by the peculiarities of the binding of calcium ions in the presence of a fungicidal modifier.

## 1 Introduction

Currently, the problem of ensuring biosafety in public, industrial and private buildings and structures are becoming increasingly important. This is due to an increase in the number of diseases caused by exposure to spores of mold fungi and mycotoxins [1-3]. The problem can be solved, at least partially, in case of application of building materials which contain fungicidal modifiers. The newly developed modifiers for building materials should be safe and also should provide the means for bulk modification. One of such modifiers is the product of precipitation of sodium hydrosilicates with a solution of zinc sulfate [4].

The fungicidal modifier can be synthesized by precipitation of sodium hydrosilicates with an aqueous solution of zinc sulfate at different  $v(\text{Zn})/v(\text{Si})$  ratios (from 0.8 to 1.0). It is known that the chemical composition of the fungicidal modifier can be represented by the amorphous part (zinc hydrosilicates and silicic acid) that contains crystalline  $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$  in various ratios depending on  $v(\text{Zn})/v(\text{Si})$  [5]. It is obvious that such

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modifier may affect both rheological characteristics of gypsum paste and structure of hardened gypsum stone.

The aim of the work was to investigate the effect of the fungicidal modifier based on zinc hydrosilicates on the structural features of the gypsum stone.

## 2 Materials and methods

Construction gypsum of grade G5 was used during the study. This gypsum meets the requirements of RU GOST 125-79. For such gypsum the start of setting time is 8 minutes 30 seconds, end of setting time is 13 minutes, normal density of the gypsum paste is 62% and compressive strength of the stone is 14 MPa.

Zinc hydrosilicates were synthesized by precipitating of sodium silicate by the solution of zinc sulfate. The  $v(\text{Zn})/v(\text{Si})$  ratio was varied in 0.8...1.0 range. The precipitation products were washed from sodium sulfate with distilled water and then dried and grinded. Zinc hydrosilicate powder was combined with gypsum in an amount from 0.5 to 3.0% by weight (of gypsum). Normal density and setting time of the modified gypsum paste were examined according to RU GOST regulations. The calcium concentration in the aqueous solution was determined by the complexometric method using Trilon B in the presence of eriochrome black indicator and ammonia buffer solution. To prepare the solution, 0.1 g of modified gypsum stone was dissolved in 100 ml of distilled water and kept for the necessary time. Then the solution was filtered and volume of solution was measured.

## 2 Results and Discussion

To assess the rheological properties of gypsum paste, there were performed several studies of normal density of the modified gypsum paste. The results are summarized in Table 1.

**Table 1.** Normal density of gypsum paste with zinc hydrosilicates (zinc hydrosilicates were synthesized at  $v(\text{Zn})/v(\text{Si}) = 0.8...1.0$ ).

Amount of modifier, %	Required W/G ratio
0.5	0.625
1.0	0.635
1.5	0.640
2.0	0.650
3.0	0.670

As it follows from the analysis of the data in Table 1, higher values of content of zinc hydrosilicates in the composition of the binder correspond to higher values of the normal density of gypsum paste. This can be explained both by the ability of the silicic acid, which is the part of the modifier, to bind the water, and also by the lower particle size of the modifier in comparison with gypsum. It should be noted that type of changes of the normal density of gypsum paste for all studied compositions remains the same. Therefore, the value of particle size of the biocidal modifier has a dominant effect.

The admixture of modifier has a strong effect on setting time of the gypsum paste. The values of setting time are summarized in Table 2.

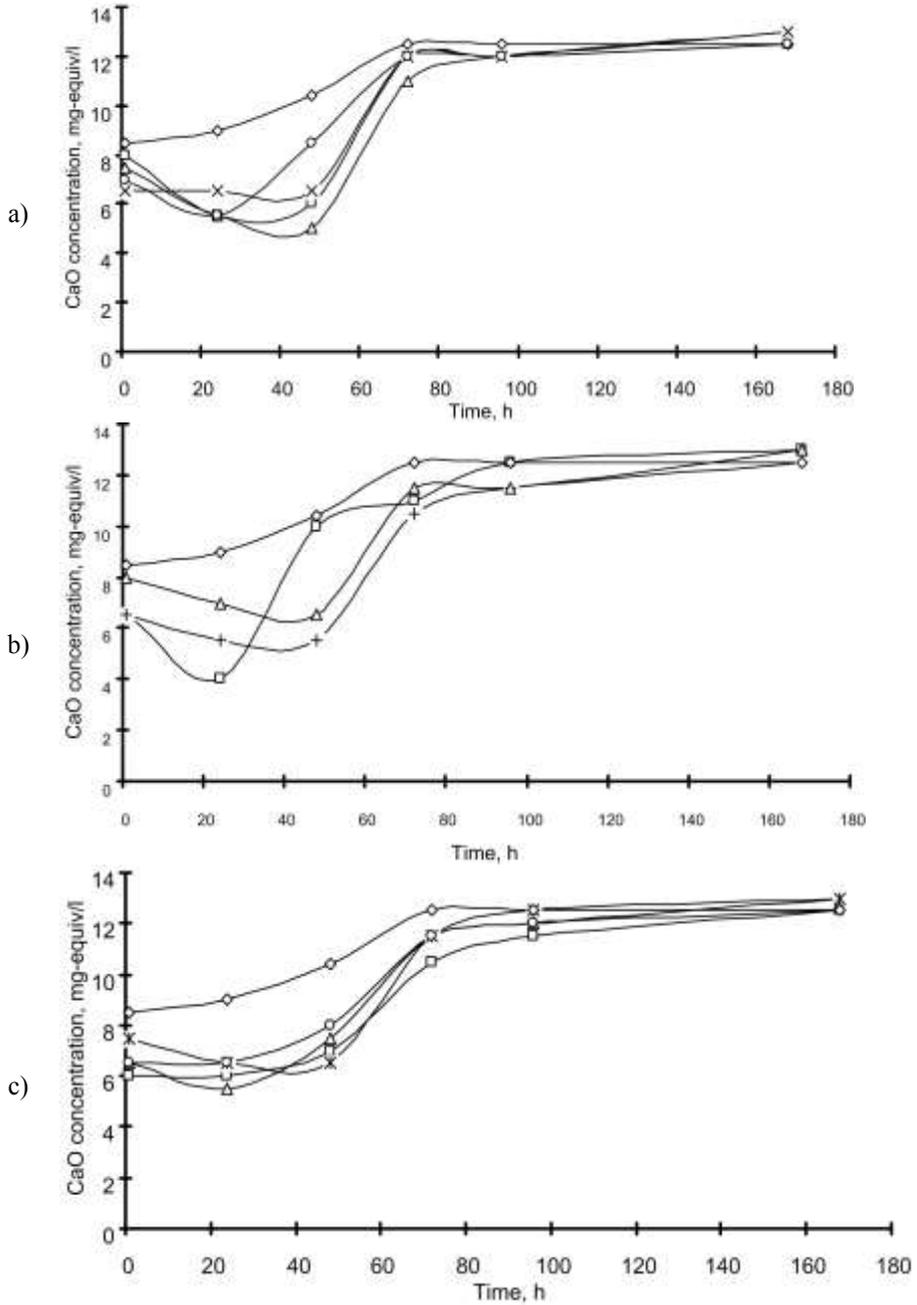
**Table 2.** Setting time.

Amount of admixture, %	Start of setting, min:s	End of setting, min:s
Zinc hydrosilicates synthesized at $v(\text{Zn})/v(\text{Si}) = 0.8$		
0.5	8:00	12:00
1.0	8:30	13:00
1.5	9:00	15:30
2.0	10:00	15:00
3.0	11:30	16:00
Zinc hydrosilicates synthesized at $v(\text{Zn})/v(\text{Si}) = 0.9$		
0.5	4:00	5:30
1.0	5:00	7:00
1.5	5:30	9:00
2.0	6:30	9:30
3.0	12:30	20:00
Zinc hydrosilicates synthesized at $v(\text{Zn})/v(\text{Si}) = 1.0$		
0.5	9:00	11:30
1.0	9:00	12:30
1.5	9:30	13:00
2.0	9:30	13:30
3.0	11:30	15:00

It follows from Table 2 that setting time lowers for compositions with zinc hydrosilicates that were synthesized at  $v(\text{Zn})/v(\text{Si}) = 0.8$  and  $v(\text{Zn})/v(\text{Si}) = 1.0$  ratios. For the  $v(\text{Zn})/v(\text{Si}) = 0.9$  ratio, two effects were observed. At low concentrations of the admixture there was a notable acceleration of setting of the gypsum paste. If the concentration of modifier is increased up to 3% by weight of gypsum, there was a significant slowdown of setting. The former slowing down of the setting with the admixture of zinc hydrosilicates that were synthesized with  $v(\text{Zn})/v(\text{Si}) = 0.8$  and 1.0 ratios can be explained by the dominant influence of the physical factor over the chemical one.

In particular, admixture of a fungicidal modifier leads to an increase in the distance between the gypsum crystals. This helps to reduce the rate of formation of bonds between the forming crystals of the gypsum stone. When using a modifier based on zinc hydrosilicates that were synthesized with the  $v(\text{Zn})/v(\text{Si}) = 0.9$  ratio, the chemical factor becomes dominant. Namely, according to [6], the silicic acid accelerates setting of binders in case of low concentrations and decelerated setting in case of relatively high concentrations. This explanation of the change in the amount of silicic acid in composition of modifier is consistent with the data concerning chemical composition that are presented in [5].

To investigate the effect of the chemical factor, the chemical composition of the modified gypsum stone was examined (Figure 1). It is known [7-16] that for the interaction of calcium-containing binders with hydrosilicates of metals, the primary method for improving the quality (compressive strength, water resistance) is the chemical interaction of calcium salts with silicic acid of modifier; such chemical interaction leads to the formation of calcium hydrosilicates. It is obvious that in this case the concentration of calcium ions in the solution should decrease.



**Fig. 1.** Concentration of CaO in the aqueous extract of gypsum modified with zinc hydrosilicates that were synthesized at  $v(\text{Zn})/v(\text{Si}) = 0.8$  (a),  $v(\text{Zn})/v(\text{Si}) = 0.9$  (b) and  $v(\text{Zn})/v(\text{Si}) = 1.0$  ratios:  $\diamond$  – control compositions;  $\square$  – 0.5% of modifier; + – 1.0% of modifier;  $\Delta$  – 1.5% of modifier;  $\times$  – 2.0% of modifier;  $\circ$  – 3.0% of modifier.

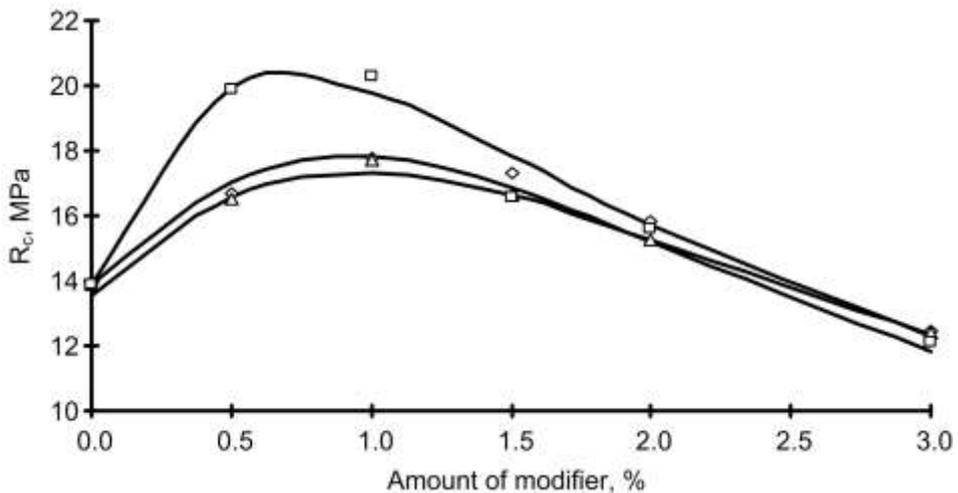
The analysis of figure 1 shows that when using zinc hydrosilicates in the composition of binder, and such hydrosilicates were obtained at, there is a significant decrease in the concentration of CaO in the initial period when the content of the modifier is 0.5% by

weight of the binder (during the first day). With an increase in the amount of modifier, the amount of bound CaO decreases.

Taking into account that in model systems binding of calcium was carried out in a relatively more dilute medium and for a long time, it can be assumed that the chemical interaction takes place only when zinc hydrosilicates were obtained at  $v(\text{Zn})/v(\text{Si}) = 0.9$  ratio and introduced into gypsum in low concentration.

This is consistent with the experimental data obtained during examination of the setting time of modified gypsum stone (Table 2). For other compounds, the chemical binding of calcium occurs at a later time, so when the mixture sets, there is no notable binding of calcium. In this case, relatively high content of silicic acid slows down the process of setting the gypsum paste. Changing the conditions of structure formation leads to a change of the structure of the formed stone, and accordingly, to a change in properties of the modified gypsum stone.

The results of the study of the effect of zinc hydrosilicates on the strength of gypsum stone show the extreme nature of the observed dependence (Figure 2).



**Fig. 2.** Compressive strength of a modified gypsum stone,  $\diamond - v(\text{Zn})/v(\text{Si}) = 0.8$ ;  $\Delta - v(\text{Zn})/v(\text{Si}) = 0.9$ ;  $\square - v(\text{Zn})/v(\text{Si}) = 1.0$ .

It is quite evident from the Figure 2 that the data can be approximated by rational regression models (control variable  $C$  is the amount of modifier, %)

$$R_c = \frac{R_0 + b_1 C}{1 + b_2 C + b_3 C^2},$$

where  $R_0$ ,  $b_1$ ,  $b_2$  and  $b_3$  – parameters (first parameter is the strength of unmodified gypsum stone). Experimentally obtained values of parameters are summarized in Table 3.

**Table 3.** Parameters of regression models of compression strength.

$v(\text{Zn})/v(\text{Si})$	$R_0$ , MPa	$b_1$ , MPa/%	$b_2$ , MPa/%	$b_3$ , MPa/(%) <sup>2</sup>
0.8	13.86	9.85	0.11	0.24
0.9	13.89	8.44	-0.07	0.26
1.0	13.87	30.46	0.60	0.64

It follows from joint analysis of Figure 2 and Table 3 that there are two processes takes place when fungicidal modifying agent based on zinc hydrosilicates is admixed to the gypsum; namely “constructive” and “destructive” processes. The value of the  $b_1$  parameter

varies in a wave-like manner with an increase of zinc content in the admixture. This indicates that the contribution of the “constructive” factor is complex.

Empirical parameters  $b_2$  and  $b_3$  are associated with “destructive” factors. The rate of “destructive” influence for  $v(\text{Zn})/v(\text{Si}) = 0.9$  is negative. It should be noted that this is consistent with the nature of the change in the setting time of the modified gypsum stone, namely – with the influence of silicic acid. The compressive strength of the obtained products of the interaction lowers, but the influence of the “destructive” factor is also reduced. This may be due to the combining of layered zinc hydrosilicates by the interaction products of silicic acid and calcium ions.

### 3 Summary

It has been shown that the rheological properties of the gypsum paste does not depend on the chemical composition of the fungicidal modifier. Such properties is mostly affected by the particle size of the modifier.

The structure formation (and resulting compressive strength) of a gypsum stone during its modification with zinc hydrosilicates depends on the chemical composition and content of the modifier. The highest setting rate is observed when chemical binding of calcium takes place at a low concentration of modifier (0.5%) and  $v(\text{Zn})/v(\text{Si})$  ratio is 0.9.

With other types and quantities of the modifier, the main mechanism that affects the structure formation of the gypsum paste is physical one and consists in creating barriers that prevent the combining of individual crystals of the gypsum hemihydrate. When a gypsum stone is formed in the presence of a fungicidal modifier that was synthesized at  $v(\text{Zn})/v(\text{Si}) = 0.9$ , there is a significant difference in structure formation process. This is consistent with the nature of the change in the setting time of the modified gypsum stone, namely – with the influence of silicic acid. The compressive strength of the obtained products of the interaction lowers, but the influence of the “destructive” factor is also reduced. This may be due to the combining of layered zinc hydrosilicates by the interaction products of silicic acid and calcium ions.

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