

# Chemical composition of nanomodified cement stone

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**Abstract.** Improving the properties of cement building materials is possible with the use of modifiers, including nanoscale ones. Such nanomodifiers include hydrosilicates of zinc and copper. The increase in the performance characteristics of nanomodified cement composites is due to changes in the chemical composition of the resulting cement stone, in particular, an increase in the content of hydrosilicate structures. The chemical composition of the cement stone was studied by FTIR-spectroscopy. Colloidal solutions of zinc and copper hydrosilicates with known characteristics were used for the nanomodification of cement stone. It is shown that when using copper hydrosilicates synthesized at high concentrations of iron hydroxide, the concentration of amorphous silica does not significantly affect the composition of cement stone. However, with a decrease in the concentration of iron hydroxide, with an increase in the concentration of amorphous silica, the content of hydrosilicate structures increases. The use of nanoscale zinc hydrosilicates is more efficient than copper hydrosilicates. Their use makes it possible to increase the content of structures containing silicon-oxygen tetrahedra, submicrocrystalline calcium hydrosilicates of a tobermorite-like structure in cement stone, and the formation of ettringite is also noted. Thus, it was found that the use of zinc hydrosilicates as nanomodifiers for cement stone allows increasing the content of hydrosilicate structures in hydration products.

## 1 Introduction

The most common method of regulating the mechanical and operational properties of building materials is the use of modifying additives [1-11]. One of the reasons for the change in properties is the change in the chemical composition of the resulting composite. For cement composites, this is realized by binding portlandite to form various hydrosilicates [12-16]. To obtain a modified cement stone, it is advisable to use colloidal solutions of metal hydrosilicates [17-20]. Such modifiers include nanoscale zinc and copper hydrosilicates that differ in cation type, concentration, and silicate modulus. Depending on

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these characteristics, nanoscale metal hydrosilicates can have different activities and have different effects on the chemical composition of cement stone.

## 2 Methods and materials

Colloidal solutions of copper and zinc hydrosilicates have been used for nanomodification of cement stone. The synthesis of the nanomodifier was carried out according to the technology described in [21]. Aggregative stability of the modifier is described in the article [21]. The chemical compositions of colloidal solutions are presented in table 1. The concentrations of colloidal solutions are presented in table 2. The average particle diameter of metal hydrosilicates is shown in table 3.

**Table 1.** Gross formulae of colloidal solutions.

$\alpha$	Concentration of $\text{Fe}(\text{OH})_3$ ( $C(\text{Fe}(\text{OH})_3)$ ), %		
	0.3	0.5	0.7
Copper hydrosilicates			
0.5	$\text{CuO} \cdot 0.86\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{CuO} \cdot 1.44\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{CuO} \cdot 2.02\text{SiO}_2 \cdot n\text{H}_2\text{O}$
1.0	$\text{CuO} \cdot 1.73\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{CuO} \cdot 2.88\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{CuO} \cdot 4.03\text{SiO}_2 \cdot n\text{H}_2\text{O}$
1.5	$\text{CuO} \cdot 2.59\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{CuO} \cdot 4.32\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{CuO} \cdot 6.05\text{SiO}_2 \cdot n\text{H}_2\text{O}$
Zinc hydrosilicates			
0.5	$\text{ZnO} \cdot 2.35\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{ZnO} \cdot 3.92\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{ZnO} \cdot 5.49\text{SiO}_2 \cdot n\text{H}_2\text{O}$
1.0	$\text{ZnO} \cdot 4.70\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{ZnO} \cdot 7.84\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{ZnO} \cdot 10.97\text{SiO}_2 \cdot n\text{H}_2\text{O}$
1.5	$\text{ZnO} \cdot 7.05\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{ZnO} \cdot 11.76\text{SiO}_2 \cdot n\text{H}_2\text{O}$	$\text{ZnO} \cdot 16.46\text{SiO}_2 \cdot n\text{H}_2\text{O}$

**Table 2.** Concentrations of solutions.

$\alpha$	Concentration of $\text{Fe}(\text{OH})_3$ ( $C(\text{Fe}(\text{OH})_3)$ ), %		
	0.3	0.5	0.7
Hydrosilicates of copper			
0.5	0.0431	0.0560	0.0688
1.0	0.0624	0.0881	0.1137
1.5	0.0816	0.1202	0.1587
Hydrosilicates of zinc			
0.5	0.0282	0.0410	0.0539
1.0	0.0474	0.0732	0.0989
1.5	0.0667	0.1053	0.1438

**Table 3.** The average particle diameter of metal hydrosilicates, nm.

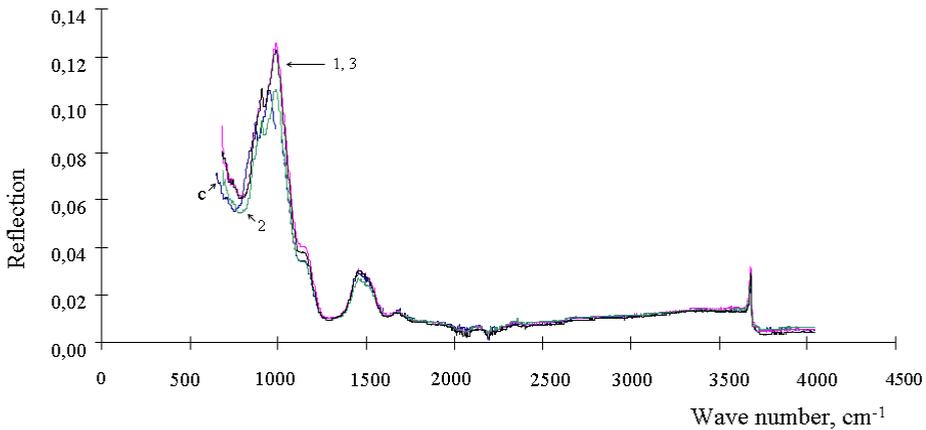
$\alpha$	Concentration of $\text{Fe}(\text{OH})_3$ ( $C(\text{Fe}(\text{OH})_3)$ ), %		
	0.3	0.5	0.7
Hydrosilicates of copper			
0.5	18.3	16.1	13.7
1.0	25.6	27.5	28.4
1.5	20.3	30.8	22.7
Hydrosilicates of zinc			
0.5	13.3	12.9	14.7
1.0	11.3	15.8	21.0
1.5	13.1	20.8	29.7

Nanomodified cement stone is obtained from cement paste with a water content of 26 % by weight of cement. Curing occurred within 28 days at a temperature of 25 °C and a humidity of 100 %. The chemical composition was analyzed using the FTIR-spectroscopy method. An Agilent Cary 630 spectrophotometer was used to obtain the spectrograms. The

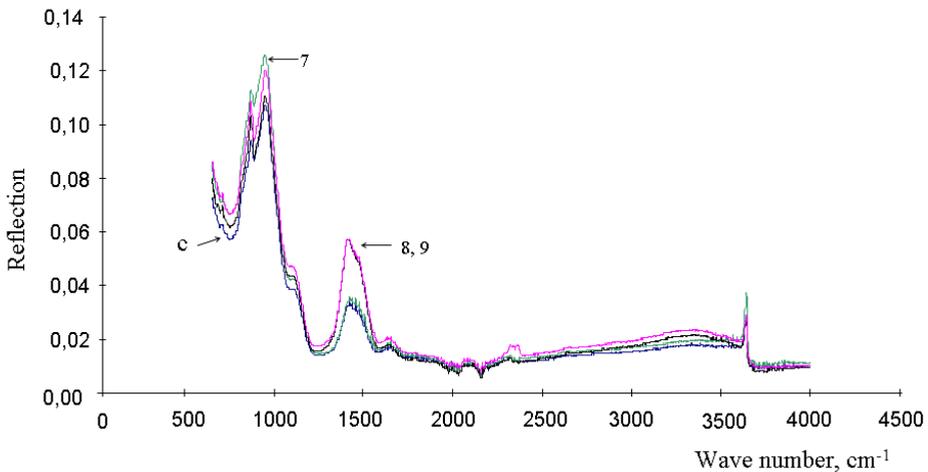
advantage of the FTIR-spectroscopy method is the ability to identify the presence of groups of atoms of compounds that are in an amorphous state, compensating for the disadvantages of X-ray phase analysis.

### 3 Results

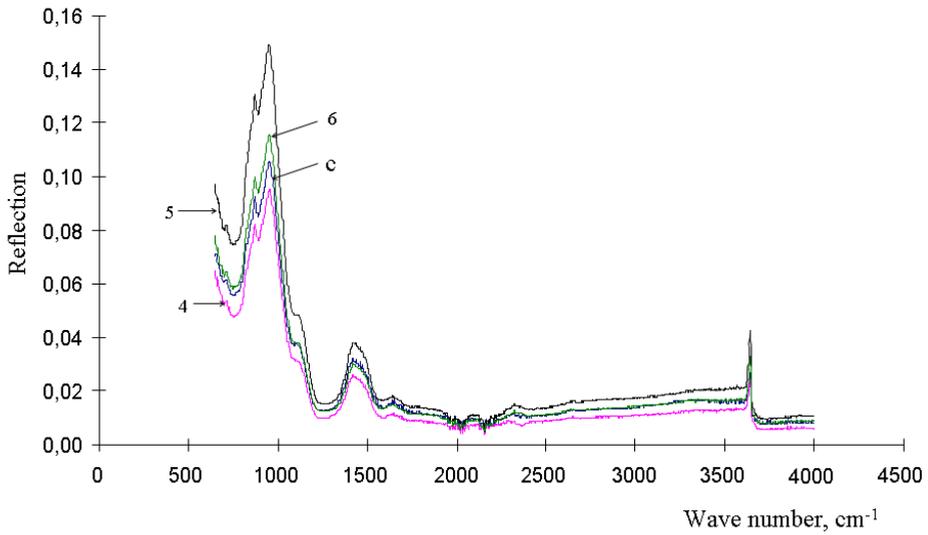
The results of the study of cement stone hydration products in the presence of nanoscale modifiers based on zinc and copper hydrosilicates are presented in Figures 1-4.



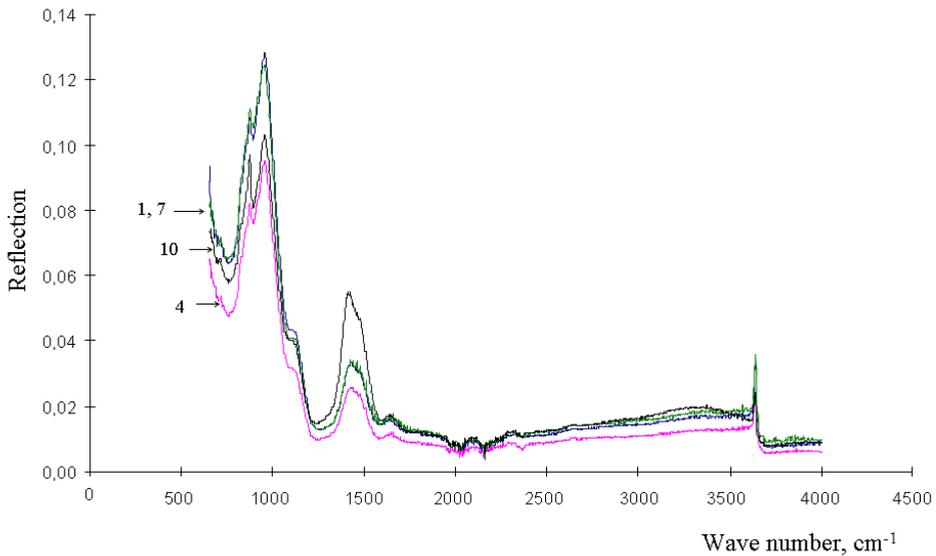
**Fig. 1.** FTIR-spectrogram of cement stone modified with nanoscale copper hydrosilicates synthesized at  $C(\text{Fe}(\text{OH})_3) = 0.7\%$ : 1 –  $\alpha = 0.5$ ; 2 –  $\alpha = 1.0$ ; 3 –  $\alpha = 1.5$ ; c – control composition



**Fig. 2.** FTIR-spectrogram of cement stone modified with nanoscale copper hydrosilicates synthesized at  $C(\text{Fe}(\text{OH})_3) = 0.5\%$ : 7 –  $\alpha = 0.5$ ; 8 –  $\alpha = 1.0$ ; 9 –  $\alpha = 1.5$ ; c – control composition



**Fig. 3.** FTIR-spectrogram of cement stone modified with nanoscale zinc hydrosilicates synthesized at  $C(Fe(OH)_3) = 0.7\%$ : 4 –  $\alpha = 0.5$ ; 5 –  $\alpha = 1.0$ ; 6 –  $\alpha = 1.5$ ; c – control composition



**Fig. 4.** FTIR-spectrogram of cement stone modified with nanoscale hydrosilicates: compositions numbered 1, 4, and 7 correspond to the compositions shown in Figures 1-3; 10 – zinc hydrosilicates synthesized at  $C(Fe(OH)_3) = 0.7\%$  and  $\alpha = 0.5$

## 4 Discussion

The analysis of the obtained spectrograms shows that they have a general appearance characteristic of the results of the analysis of cement stone. The spectrograms have responses at wave number  $3644\text{ cm}^{-1}$ , an elongated weakly expressed response at  $3300\dots3500\text{ cm}^{-1}$ , weakly expressed responses at  $2335\dots2350\text{ cm}^{-1}$  and  $1662\dots1670\text{ cm}^{-1}$ , a response at wave numbers  $1469\dots1483\text{ cm}^{-1}$ , which has an overlap with the response at

1426...1450  $\text{cm}^{-1}$ . There is also a partial response at a wave number of 1122...1126  $\text{cm}^{-1}$ , which is aligned with the response at a wave number of 952...960  $\text{cm}^{-1}$ . There is also a response at a wave number of 876...878  $\text{cm}^{-1}$ . The presence of a band at a wave number of 3640...3645  $\text{cm}^{-1}$  is caused by vibrations of free hydroxyl groups. Therefore, the response may belong to water, portlandite, some hydrosilicates with a certain structure relative to the position of the hydroxyl group. It is presented on all spectrograms. The presence of an elongated response at a wave number of 3300...3500  $\text{cm}^{-1}$  indicates the water content of the cement stone. Also, a small response at a wave number of 1662...1670  $\text{cm}^{-1}$  also indicates the presence of water.

It should be noted that these anomalies are weakly expressed on the spectrograms. The most clearly indicated anomalies are observed for compositions nanomodified with copper hydrosilicates obtained at  $C(\text{Fe}(\text{OH})_3) = 0.5\%$ ,  $\alpha = 1.0$  and  $1.5$ ; and zinc hydrosilicates synthesized at  $C(\text{Fe}(\text{OH})_3) = 0.5\%$  and  $\alpha = 0.5$ .

So, probably, the response at the wave number 3640...3645  $\text{cm}^{-1}$  corresponds to portlandite or calcium hydrosilicates. Peaks at a wave number of 1426...1483  $\text{cm}^{-1}$  probably characterize the deformation oscillations of hydroxyl groups at the vertices of silicon-oxygen tetrahedra and also reflect the presence of calcium carbonate. In the studied samples, the existence of silicon-oxygen tetrahedra and calcium carbonate is represented in all the samples. However, the cement stone obtained using a nanomodifier based on copper hydrosilicates synthesized at  $C(\text{Fe}(\text{OH})_3) = 0.7\%$ , regardless of the value of  $\alpha$  in the studied range, has approximately equal intensity. Thus, under these conditions, the value of  $\alpha$  does not affect the content of hydrosilicates that have silicon-oxygen tetrahedra in their structure. When the concentration of iron hydroxide is reduced to  $C(\text{Fe}(\text{OH})_3) = 0.5\%$  at  $\alpha = 0.5$  changes in the amount of these hydrosilicates also do not change, but at  $\alpha = 1.0$  and  $1.5$ , the content of hydrosilicate structures increases significantly. The use of nanoscale zinc hydrosilicates makes it possible to increase the amount of calcium hydrosilicates containing silicon-oxygen tetrahedra only when using a nanomodifier synthesized at  $C(\text{Fe}(\text{OH})_3) = 0.7\%$  at  $\alpha = 1.0$ . When the value of  $\alpha$  decreases to  $0.5$ , the intensity of the described response decreases, and when the value of  $\alpha = 1.5$ , the content of hydrosilicates having silicon-oxygen tetrahedra in their structure is comparable to their content in the control composition. The effect of the cation of nanoscale hydrosilicates on the content of silicon-oxygen tetrahedra was evaluated by comparing the response intensity of the spectrograms of the compositions of zinc and copper hydrosilicates obtained at  $C(\text{Fe}(\text{OH})_3) = 0.5$  and  $0.7\%$  and  $\alpha = 0.5$ . Analysis of the spectrogram of Figure 4 shows that the introduction of nanoscale zinc hydrosilicates synthesized at  $C(\text{Fe}(\text{OH})_3) = 0.7\%$  and  $\alpha = 0.5$ , leads to a significant increase in the content of hydration products having silicon-oxygen tetrahedra in their structure. In addition, the combination of a band with a wave number of 1426...1439  $\text{cm}^{-1}$  and a wide band of the spectrum in the region of the band numbers of 3300...3500  $\text{cm}^{-1}$  may also indicate the presence of submicrocrystalline calcium hydrosilicates like as a tobermorite structure. The response at a wave number of 1122...1126  $\text{cm}^{-1}$  is weakly expressed for all the studied compositions and indicates the oscillation of the Si – O – Si center, symmetric and asymmetric Si – O oscillations characteristic of tobermorite-like structures. Responses in the wave number range 800...1100  $\text{cm}^{-1}$  are typical for calcium hydrosilicates. At a wave number of 976...958  $\text{cm}^{-1}$ , three types of Si(OH) valence vibrations are observed, as well as vibrations of groups of calcium hydrosulfoaluminates (ettringite). The maximum at the wave number 887...890  $\text{cm}^{-1}$  is typical for  $-(\text{Si}_4\text{O}_{10})_\infty$  and also for ettringite.

The intensity of responses at the indicated wavenumbers is observed when using nanosized copper hydrosilicates synthesized at  $C(\text{Fe}(\text{OH})_3) = 0.5$  and  $0.7\%$ ,  $\alpha = 0.5$  and  $\alpha = 1.5$ , as well as zinc hydrosilicates, obtained at  $C(\text{Fe}(\text{OH})_3) = 0.7\%$ :  $\alpha = 1.0$ .

## 5 Conclusion

The use of nanoscale zinc hydrosilicates is more efficient than copper hydrosilicates. Their use makes it possible to increase the concentration of structures containing silicon-oxygen tetrahedra, submicrocrystalline calcium hydrosilicates of a tobermorite-like structure in cement stone, and the formation of ettringite is also noted. Thus, it was found that the use of zinc hydrosilicates as nanomodifiers for cement stone allows increasing the content of hydrosilicate structures in hydration products.

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