Study of the phase composition of nanomodified biocidal cement stone by X-ray analysis

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Abstract. Due to high importance of cement concrete for construction industry it is essential to discover new ways towards increasing the durability of the concrete. The problem of low durability is of highest significance in case of hot and humid operating conditions. We have discovered that some biocidal modifiers are able to not only to solve their primary objective, but also may lead to higher resistance of concrete since they change the chemical composition of the cement stone. The results of the study of cement stone by X-ray phase analysis are presented in the article. It has been established that zinc hydrosilicates slow down the hydration of cement, and, thus, can successfully be used as agents which lead to increase of the concrete’s durability in hot climate.

1. Introduction
Improving the durability of building materials is an important task [1, 2]. The operation of cement composites at high humidity and temperature often leads to their rapid destruction. Destruction is often caused by microorganisms [3, 4]. Microorganisms can not only destroy building materials, but also harm human health. Therefore, it is necessary to use biocidal modifiers in the composition of building materials [5]. Nanosized hydrosilicates of zinc and copper are biocidal modifiers with good aggregative stability. Nanomodification of cement-based building materials with similar sols leads to a change of their chemical composition [6, 7, 8, 9]. Therefore, it is important to study the chemical composition of nanomodified 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 [10]. Aggregative stability of the modifier is described in the article [10].

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.

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 phase composition of nanomodified cement stones is determined using a Shimazu XRD 6000 diffractometer in K-α-Cu radiation.
### Table 1. Gross formulae of colloidal solutions.

| α   | Concentration of Fe(OH)$_3$, % | Copper hydrosilicates                                      | Zinc hydrosilicates                                      |
|-----|-------------------------------|-----------------------------------------------------------|----------------------------------------------------------|
|     |                               | CuO·0.86SiO$_2$·nH$_2$O                                   | ZnO·2.35SiO$_2$·nH$_2$O                                  |
| 0.5 | 0.3                           | CuO·1.44SiO$_2$·nH$_2$O                                   | ZnO·3.92SiO$_2$·nH$_2$O                                  |
| 1.0 | 0.5                           | CuO·2.88SiO$_2$·nH$_2$O                                   | ZnO·7.84SiO$_2$·nH$_2$O                                  |
| 1.5 | 0.7                           | CuO·4.32SiO$_2$·nH$_2$O                                   | ZnO·11.76SiO$_2$·nH$_2$O                                 |

### Table 2. Concentrations of solutions.

| α   | Concentration of Fe(OH)$_3$, % | Concentrations of solutions                               |
|-----|-------------------------------|-----------------------------------------------------------|
|     |                               | Hydrosilicates of copper                                   |
|     |                               | Hydrosilicates of zinc                                     |
|     |                               |                                                            |
| 0.5 | 0.3                           | 0.0431                                                    |
|     |                               |                                                            |
| 1.0 | 0.5                           | 0.0624                                                    |
|     |                               |                                                            |
| 1.5 | 0.7                           | 0.0816                                                    |
Table 3. The average particle diameter of metal hydrosilicates, nm.

| α  | Concentration of Fe(OH)₃, % | 0.3  | 0.5  | 0.7  |
|----|-----------------|------|------|------|
| 0.5| Hydrosilicates of copper | 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       | 13.3 | 12.9 | 14.7 |
| 0.5|                               | 11.3 | 15.8 | 21.0 |
| 1.0|                               | 13.1 | 20.8 | 29.7 |

3. Results
The results of the study demonstrate the presence of crystalline and amorphous substances in the composition of nanomodified cement stone. We analyze all the obtained X-ray data. The crystalline phase contains cement clinker and hydration products. Diffuse halo in the range (2Ѳ) 25-35° indicates the presence of amorphous substances. X-ray analysis demonstrates the presence of ettringite and portlandite in various concentrations in the composition of all cement stones. Non-hydrated alite is also present in all cement stones. The main maximum of alite (d = 3.04 Å) coincides with the anomalies of other silicates, for example xonotlite, riverside, CSH (I) and CSH (II), tobermorites and others. There is a small amount of belite and calcium alumino ferrite in the composition of nanomodified cement stone. Calcium sulfate hemihydrate is fully depleted due to chemical transformations. Low amount of calcium carbonate is found.

At the same time, distinctive features can be observed in several XRD patterns. This allows to compare the phase composition of nanomodified cement stones when a certain factor varies. A decrease in the concentration of ettringite occurs with an increase in the concentration of silicic acid in the nanomodifier. The concentration of portlandite grows with an increase in the content of silicic acid. A decrease in the concentration of portlandite can occur due to the formation of new substances, for example, calcium hydrosilicates. The results of the phase composition studies are presented in figure 1. With an increase in the amount of silicic acid, the binding of portlandite is blocked. Content of alit does not change significantly.
Figure 1. X-ray diffraction patterns of cement stone modified with copper hydrosilicates (Fe(OH)$_3$ = 0.7); 1 – $\alpha$ = 0.5; 2 – $\alpha$ = 1.0; 3 – $\alpha$ = 1.5; a – alite; b – belite; p – portlandite; e – ettringite; af – calcium aluminoferrite.

An increase in the concentration of ettringite and a decrease in the concentration of portlandite at d = 4.91 Å occurs in case of a decrease in the concentration of sol of iron hydroxide and an increase in the concentration of silicic acid. The maximum at d = 3.04 Å is higher than for composition 8 with an intermediate concentration of silicic acid (figure 2).

Figure 2. X-ray diffraction patterns of cement stone modified with copper hydrosilicates (Fe(OH)$_3$ = 0.5); 7 – $\alpha$ = 0.5; 8 – $\alpha$ = 1.0; 9 – $\alpha$ = 1.5 a – alite; b – belite; p – portlandite; e – ettringite; af – calcium aluminoferrite.
An increase in the concentration of ettringite in all compositions is observed when the concentration of sol of iron hydroxide is decreased. This observed most clearly for composition 15 (figure 3).

**Figure 3.** X-ray diffraction patterns of cement stone modified with copper hydrosilicates (Fe(OH)$_3$ = 0.3); 13 – $\alpha$ = 0.5; 14 – $\alpha$ = 1.0; 15 – $\alpha$ = 1.5; a – alite; b – belite; p – portlandite; e – ettringite; af – calcium aluminoferrite.

The minimum concentration of portlandite is observed at $\alpha$ = 0.5 (Fe(OH)$_3$ = 0.3).

But the response intensity at $d$ = 3.04 Å slightly exceeds the average values. Thus, probably, a slowdown in cement hydration is occurred.

The content of tobermorite increases with increasing concentration of iron hydroxide. This is a consequence of the effect of iron hydroxide on the rate of cement hydration at higher concentrations of silicic acid, which increases the concentration of tobermorite.

When using zinc hydrosilicates (figure 4), a high concentration of tobermorite in the composition of the cement stone is also noted. But with a high concentration of iron hydroxide sol and the use of zinc cation, a decrease in the content of portlandite occurs with an increase in the concentration of silicic acid. The response intensity at $d$ = 3.04 Å varies significantly. And the response at $d$ = 2.61 Å changes only slightly. At $d$ = 2.78 Å, a higher maximum intensity is observed for composition 6.

Thus, a partial slowdown of hydration processes and the binding of portlandite to calcium hydrosilicates occur. The formation of ettringite occurs in all the described compositions modified with zinc hydrosilicates.

Hydration retardation processes (composition 10) occur when using an iron hydroxide sol C(Fe(OH)$_3$) = 0.5% and a low concentration of silicic acid. This is confirmed by the relative intensity of other anomalies belonging to alite, for example, at $d$ = 2.78 Å (figure 5). As the content of silicic acid increases, the degree of cement hydration increases. An increase in the response intensity at $d$ = 4.91 Å indicates this. At a low concentration of silicic acid in the composition of the cement stone, a high content of ettringite is noted. Changes in the concentration of tobermorite are complex.
Figure 4. X-ray diffraction patterns of cement stone modified with zinc hydrosilicates \((\text{Fe(OH)}_3 = 0.7)\): 4 – \(\alpha = 0.5\); 5 – \(\alpha = 1.0\); 6 – \(\alpha = 1.5\); a – alite; b – belite; p – portlandite; e – ettringite; af – calcium aluminoferrite.

Figure 5. X-ray diffraction patterns of cement stone modified with zinc hydrosilicates \((\text{Fe(OH)}_3 = 0.5)\): 10 – \(\alpha = 0.5\); 11 – \(\alpha = 1.0\); 12 – \(\alpha = 1.5\); a – alite; b – belite; p – portlandite; e – ettringite; af – calcium aluminoferrite.

A high alite content and a low concentration of portlandite are observed in compositions with a low concentration of iron hydroxide sol \((C(\text{Fe(OH)}_3) = 0.3\%)\). This indicates the chemical binding of portlandite and the formation of hydrosilicate structures. This can be observed in composition 16. In the samples of cement stone, a high content of ettringite is found (composition 17, figure 6).
Figure 6. X-ray diffraction patterns of cement stone modified with zinc hydrosilicates (Fe(OH)$_3$ = 0.3); 16 – $\alpha = 0.5$; 17 – $\alpha = 1.0$; 18 – $\alpha = 1.5$; a – alite; b – belite; p – portlandite; e – ettringite; af – calcium aluminoferrite.

4. Conclusion
Cement hydration retardation processes are observed when only zinc hydrosilicates are used as a nanomodifier. Thus, the specified nanomodifier in comparison with copper hydrosilicates, has advantages when used in hot climates.

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