Changes in the structural and phase composition and strength characteristics of concrete during liquid corrosion in chloride-containing media

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Abstract. The results of physico-chemical studies that allow us to judge the changes occurring in the cement stone under the influence of liquid chloride-containing media are analysed. Samples of CEM I 42.5N Portland cement with a water-cement ratio of W/C = 0.3 were exposed to solutions of 2 % MgCl₂, 0.001 % HCl and 0.1 % CaCl₂ for 150 days. Changes in the strength characteristics of CEM I 42.5N Portland cement samples under the influence of chloride-containing media were studied. It is established that the 2 % MgCl₂ solution is an extremely aggressive medium in the conditions of liquid corrosion of concrete, its action causes a deterioration in the strength characteristics of concrete by 1.5 times. The changes in the structural and phase composition of concrete that occur under the influence of chloride-containing media are studied. The relationship between the characteristics of the cement stone structure and the strength parameters of the cement stone is established. The decrease in the strength of cement concrete is associated with the decomposition of calcium hydrosilicate C₂S₂H under the influence of liquid aggressive chloride-containing media, as evidenced by the decrease in intensity and the disappearance of the lines corresponding to this compound on X-ray images.

1. Introduction

Traditionally, structural and non-structural factors affecting the performance of buildings were considered as separate issues [1-5]. But it is important to consider not only the mechanical load, as each structure is exposed to the environment, which can have a huge impact on the service life of the product.

The hydrated components (C-S-H, portlandite, sulfoaluminates) in the cement matrix are in equilibrium with the pore liquid, which is characterized by a high pH, due to the presence of OH⁻ ions (hydroxides with Na⁺ and K⁺ ions are formed). When concrete is exposed to acidic solutions, these components can dissolve at a rate that depends on the concrete's permeability, concentration, and type of acid [6-8].

The impact of chloride ions on concrete is the main cause of premature corrosion of concrete and reinforced concrete products and structures [9-12]. The risk of corrosion increases as the chloride content in the environment surrounding the concrete increases. However, only water-soluble chlorides contribute to corrosion; some acid-soluble chlorides may be bound by concrete fillers and are...
unavailable to promote corrosion. The conversion rate of acid-soluble chlorides to water-soluble ones can vary from 0.35 to 0.90, depending on the composition and operating conditions of the concrete. The water-soluble limit of chlorides is 0.15 % by weight of cement [13, 14].

In general, Portland cement concrete does not have good acid resistance. In fact, no hydraulic cement concrete, regardless of its composition, will withstand prolonged exposure to solutions with a pH of 3 or lower [15]. However, concrete can withstand the action of some weak acids, especially if the impact is accidental [16, 17].

The acids react with the calcium hydroxide of hydrated Portland cement. In most cases, as a result of a chemical reaction, water-soluble calcium compounds are formed, which are then leached with aqueous solutions [18, 19].

The mineralogical composition of cement is represented by the following clinker minerals: alite C\textsubscript{3}S (3CaO·SiO\textsubscript{2}); belite C\textsubscript{2}S (2CaO·SiO\textsubscript{2}); tricalcium aluminate C\textsubscript{3}A (3CaO·Al\textsubscript{2}O\textsubscript{3}); brownmillerite or four-calcium aluminoferite C\textsubscript{4}AF (4CaO·Al\textsubscript{2}O\textsubscript{3}·Fe\textsubscript{2}O\textsubscript{3}). Gypsum stone in cement is represented by a mineral dihydrous calcium sulfate CaSO\textsubscript{4}·2H\textsubscript{2}O. Numerous studies have shown that the main carriers of the mechanical strength of cement stone are the hydration products C\textsubscript{3}S and C\textsubscript{3}A, that is, calcium hydrosilicates [20-26].

Even after 70 years of experience in combating corrosion of reinforced concrete structures, there is a need to study the factors and parameters that affect the corrosion of reinforced concrete, and to develop or supplement standards and norms, emphasizing the need to ensure the durability of the structure.

2. Materials and methods

When studying the properties of materials, Portland cement with a normalized composition without mineral additives of the CEM I 42,5N brand was used as a binder. The choice of this brand of Portland cement is not accidental, as it is widespread and in demand in the domestic market of Russia. The chemical composition of Portland cement of the CEM I 42,5N brand, established by the quality certificate, is presented in Table 1, the mineralogical composition is given in Table 2.

| Table 1. Chemical composition of Portland cement CEM I 42,5N brand, %. |
| --- |
| SiO\textsubscript{2} | Al\textsubscript{2}O\textsubscript{3} | Fe\textsubscript{2}O\textsubscript{3} | CaO | MgO | SO\textsubscript{3} | R\textsubscript{2}O | other impurities |
| 21.55 | 5.55 | 4.7 | 62.93 | 0.76 | 2.37 | 0.54 | 1.6 |

| Table 2. Content of the main minerals of Portland cement CEM I 42,5N brand, %. |
| --- |
| C\textsubscript{3}S | C\textsubscript{3}A | C\textsubscript{2}S | C\textsubscript{4}AF | TEA |
| 68.1 | 11.0 | 8.7 | 11.9 | 0.3 |

The study of corrosion resistance was carried out on samples-cubes with a side length of 3 cm, made of Portland cement of the CEM I 42,5N brand with a water-cement ratio of W/C = 0.3. The samples were made from solutions of normal density. After 28 days of pre-hardening under normal conditions, they were immersed for 150 days in containers with a volume of 3000 cm\textsuperscript{3}, filled with solutions of 2 % MgCl\textsubscript{2}, 0.001 % HCl and 0.1 % CaCl\textsubscript{2}.

The choice of electrolytes is due to the high activity of chloride ions, which create an aggressive environment for concrete (Table 3).

| Table 3. Main characteristics of aggressive media. |
| --- |
| Compound | Molar mass, g/mol | Concentration, % | pH | Density, kg/m\textsuperscript{3} |
| MgCl\textsubscript{2} | 94 | 2 | 5.6 | 1015 |
| HCl | 36.5 | 0.001 | 5 | 998.2 |
| CaCl\textsubscript{2} | 110 | 0.1 | 6.1 | 1007 |

X-ray images were taken from crushed cement stone samples pressed into a tablet at the X-ray wavelength λ = 1.5405 Å. The essence of qualitative radiographic analysis is reduced to the
comparison of experimentally determined values of interplanar distances, lines and their intensity with reference radiographs. Phase identification after obtaining the X-ray image begins with finding the diffraction angles $2\theta$ and the corresponding interplane distances, as well as the relative intensity of each line. Based on the value of the angle $\theta$ found for each peak at a known wavelength $\lambda$ of the X-ray radiation used, the values of the interplanar distance $d$ are determined according to the Wolfe-Bragg’s equation:

$$d = \frac{\lambda}{2 \sin \theta}$$  \hspace{1cm} (1)

### 3. Results and discussion

Table 4 shows the results of strength tests of Portland cement samples exposed to various chloride-containing media for 150 days. Obviously, for samples without special additives, the most aggressive medium is a 2% MgCl$_2$ solution, which has a stronger effect on reducing the strength characteristics.

| Type of aggressive media | Breaking stress, MPa |
|-------------------------|---------------------|
| Before exposure         | 35.78               |
| 2 % solution MgCl$_2$   | 22.54               |
| 0.001 % solution HCl    | 30.41               |
| 0.1 % solution CaCl$_2$ | 28.64               |

Since there is a close relationship between the structure and the fracture mechanics of cement stone, an important aspect of research is the study of structural and phase changes occurring in cement stone under the influence of aggressive media. X-ray analysis allows us to qualitatively determine the phase composition of the cement stone. Each crystalline substance is characterized by its own set of specific lines on the radiograph. The radiographs of the samples are compared either with the radiographs of the constituent minerals or with known tabular data.

Figure 1 shows X-ray images of a cement stone sample that has not been exposed to an aggressive environment. The most pronounced lines are alite C$_3$S ($d = 3.05464; 2.72956; 1.92669$ and $1.523$ Å), belite C$_2$S ($d = 3.39$ and $2.748$ Å) and brownmillerite C$_4$AF ($d = 3.27879; 2.64102$ and $2.52309$ Å).
Figure 2 shows X-ray images of cement stone samples exposed to aggressive media: 2% MgCl$_2$ aqueous solution; 0.001% HCl aqueous solution; 0.1% CaCl$_2$ aqueous solution. X-ray images show that after finding the cement stone in an aggressive environment, there is a change in the intensity of some lines, as well as the appearance of new ones.

The decrease in the intensity and disappearance from the X-ray images of the lines corresponding to the calcium hydrosilicate C$_2$SH confirms the data of strength tests of cement samples after exposure to aggressive media (Table 4). With an increase in the aggressiveness of the medium, the structural phase-calcium hydrosilicate C$_2$SH becomes less, but the intensity of the lines corresponding to the C$_3$S alite increases. Figure 2-b shows that a line corresponding to the maximum intensity of calcium hydrosilicate C$_2$SH appears, the same line, but of a lower intensity, is present in Figure 2-b, and this line is not present in Figure 2-a.
The average decrease in the intensity of the lines of alite $C_3S$ on X-ray images is 20%, belite $C_2S$ is 12%, tricalcium aluminate $C_3A$ is 16%, four-calcium aluminoferrite $C_4AF$ is 20%, gypsum $CaSO_4\cdot2H_2O$ is 10%.

Thus, the methods of X-ray phase analysis can establish the relationship between the characteristics of the structure of the cement stone and the strength parameters of the cement stone. X-ray images prove that the real long-term strength and crack resistance of cement stone and concrete is determined not only by the porosity and degree of hydration, but also by the characteristics of the dispersed-crystallite structure of cement stone.

4. Summary

After exposure to the cement concrete with 2% $MgCl_2$ solution for 150 days, the strength of the sample decreased by 1,5 times. This concentration of chloride ions is extremely aggressive to concrete. Under the influence of 0,1% $CaCl_2$ solution, the strength of concrete decreased by 1,25 times, and under the influence of 0,001% HCl solution by 1,2 times.

The decrease in the calculated stress of concrete destruction is associated with structural and phase transformations occurring in the cement stone under exposure of a aggressive environment.

Based on the data of X-ray diffraction analysis, it was found that of the structural components of the studied brand of Portland cement CEM I 42,5N alite is more easily decomposed during concrete corrosion in liquid chloride-containing media and has the main effect on the change in the strength characteristics of concrete.

5. References

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