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The effect of added finely dispersed calcite on the corrosion resistance of cement compositions

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Abstract. Many types of the corrosion of Portland cement stone immersed into inorganic liquid media are conditioned by chemical exchange reactions between the substances dissolved in them and cement hydration products. To prevent the corrosion formation in corrosive media it is necessary to form cement clinker hydration products that do not enter into ion exchange reactions in the solutions. The concrete structure defines the penetration rate of corrosive ions and that of the removal of corrosion products, in other words the behavior of corrosive processes. The investigations that were carried out showed that the presence of finely dispersed organogenic calcite (chalk) in the cement stone composition results in a change of the phase composition of the hydrates of new formations, i.e. it results in a decreased content of the free calcium hydroxide and the binding of aluminate phases to form stable hydration products. The use of this additive contributes also to the compaction of the microstructure of cement stone due to the occupation by additive grains of the vacancies in the gaps between the cement grains and due to an increased dispersion of hydration products for which calcite particles serve as crystallization centers. All these factors contribute to an increased corrosion resistance of the cement stone and the concrete exposed to the action of corrosive solutions.

1. Introduction

The corrosion resistance of concrete depends on the phase composition of cement stone, because the solubility and reactivity of its individual phases differ significantly. The corrosion processes that occur in concrete structures exposed to the action of sea water, corrosive underground sewage water that contain chlorides, sulfates and magnesium ions depend on the interaction of these ions with hydroxide and cement stone calcium hydroaluminates. In this case, the volume of reaction products that are formed from the volume unit of the component of reacting cement stone can be increased by a factor of 2 to 5. It conditions the development of internal stress and the crack formation and it results in the corrosion damage of the structure. The rate of corrosion processes is defined by the penetration rate of corrosive ions and the rate of removal of corrosion products that is defined in its turn by the concrete structure.

One of the methods of an increase in the corrosion resistance of concrete is the filling of the matrix of cementing binder with mineral additives, i.e. finely dispersed mineral particles of a different nature



and fraction composition [1-3]. The use of the local mineral raw material as the additives provides the cost price reduction of the material and the use of the production waste assists in the solution of the issues relating to the environmental protection. A decrease in the amount of cement in the concrete mixture and a partial replacement of it by the additives whose production requires a minimum energy input results in a decrease of the total energy capacity of the production of this composite material.

The carbonate rocks [4, 5] that have chemical affinity to the cement with the particle size very similar to that of cement particles found a wide application in the construction industry as mineral additives. It conditions their physical and chemical interaction with clinker minerals and contributes to the formation of crystallization contacts with new cement formation at microstructure levels [6, 7], providing thus an improvement of the service properties of concrete. The use of finely dispersed additives contributes to the formation of more dense structure that provides a decrease in the effective diffusion coefficient of corrosive ions.

2. Experimental program

The purpose of this research was to study the influence of the addition of highly dispersed calcite (chalk) on the structure formation of the cement stone and concrete corrosion resistance.

To study the interaction character of the added highly-dispersed chalk with the Portland cement minerals and the products of their hydration we prepared the specimens consisting of clinker minerals and highly-dispersed chalk of a different component ratio. The specimens of hydrated mixtures, in particular 1 – $C_3A + C_3S + \text{gypsum}$ (0.5:9:0.5); 2 – $C_3A + C_3S + \text{gypsum} + \text{chalk}$ (1:7.5:0.5:1); 3 – $C_3A + C_3S + \text{gypsum} + \text{chalk}$ (1:6.5:0.5:2); 4 – $C_3A + \text{gypsum} + \text{chalk} + \text{CaO}$ (5:0.5:3:1.5); 5 – $C_3A + C_3S + \text{chalk}$ (0.7:5.3:4) were analyzed including Portland cement with the addition of highly-dispersed chalk with the ratio of 9:1, 8:2, 7:3, 6:4. The highly-dispersed chalk was added in the form of suspension.

Influence of added highly-dispersed chalk on the phase composition and the structure of cement stone was studied using the electron-microscopic structure analysis. Cleavages of the specimens of cement stone were made to analyze them using the scanning electron microscope JSM-6390/6390LV (Japan). Electron microscopic images were obtained at a voltage of 15 kV and the magnification of $\times 300$, $\times 1000$, $\times 2000$ and $\times 3000$.

3. Results and discussion

According to the data [8], the hydration of aluminum-containing clinker minerals of C_3A and C_4AF in the presence of calcium carbonate results in a change of the phase composition of new formations represented by calcium hydroaluminate $3CaO \times Al_2O_3 \times 6H_2O$ and the complex compound of calcium hydrocarbon aluminate (CHCA) $C_3A \times CaCO_3 \times 11H_2O$. The analysis of chemical reactions and the values of their free Gibbs energy ΔG showed that all hydration reactions of tricalcium aluminate C_3A are possible with the formation of crystalline hydrates of calcium hydrosulphoaluminates and hydrocarboaluminates of AFm and AFt-phases; a value of free Gibbs energy of ΔG reactions accounts for 1 mole of C_3A ; its value for similar conditions defines a probability of given reactions; the interaction reactions of C_3A with calcium carbonate with the formation of AFm and AFt-phases are thermodynamically irreversible when reacting components are present. In addition, in the alkaline environment of cement mortar the amorphous silica that covers the surface of chalk particles [9] interacts with calcium hydroxide with the formation of low-basic calcium hydrosilicates.

The electron-microscopic images (Figure 1) show that the new formations of cement stones were shaped as the plates with irregular edges and flakes that are adsorbed by the layers on the surface of cement particles due to their weak crystallization. The plates and flakes are 2 to 3 nm thick, these form individual blocks and the structure that reminds that of the natural mineral or toremborite and it allows for the creation of the dense structure of cement stone.

The surface of chalk particles is covered with amorphous silica; therefore, the carbonate component of chalk should be released for the interaction with calcium aluminate. It means that the surface silica of chalk should interact with calcium hydroxide of the liquid phase of cement stone prior to the formation of calcium hydrocarboaluminate. The images show that the availability of highly-dispersed

chalk results in the formation of low-basic calcium hydrosilicates, i.e. aster-like crystals providing thus conditions for the creation of concretes with high indices of water resistance and corrosion resistance.

Given electron-microscopic images of the cement stone confirmed that the structure of cement stone modified by 10 % of highly-dispersed chalk is rather dense. The structure includes portlandite, ettringite and calcium hydrocarboaluminate of a $3\text{CaO}\times\text{Al}_2\text{O}_3\times\text{CaCO}_3\times 10\text{H}_2\text{O}$ or $\text{CaO}\times\text{Al}_2\text{O}_3\times 3\text{CaCO}_3\times 31\text{H}_2\text{O}$ type, Figure 1, a.

The structure of specimens of the cement stone modified with 20 % and 30 % of highly-dispersed chalk is also rather dense, Figure 1, b, c. The structure of specimens of the cement stone with 40 % of chalk is less dense.

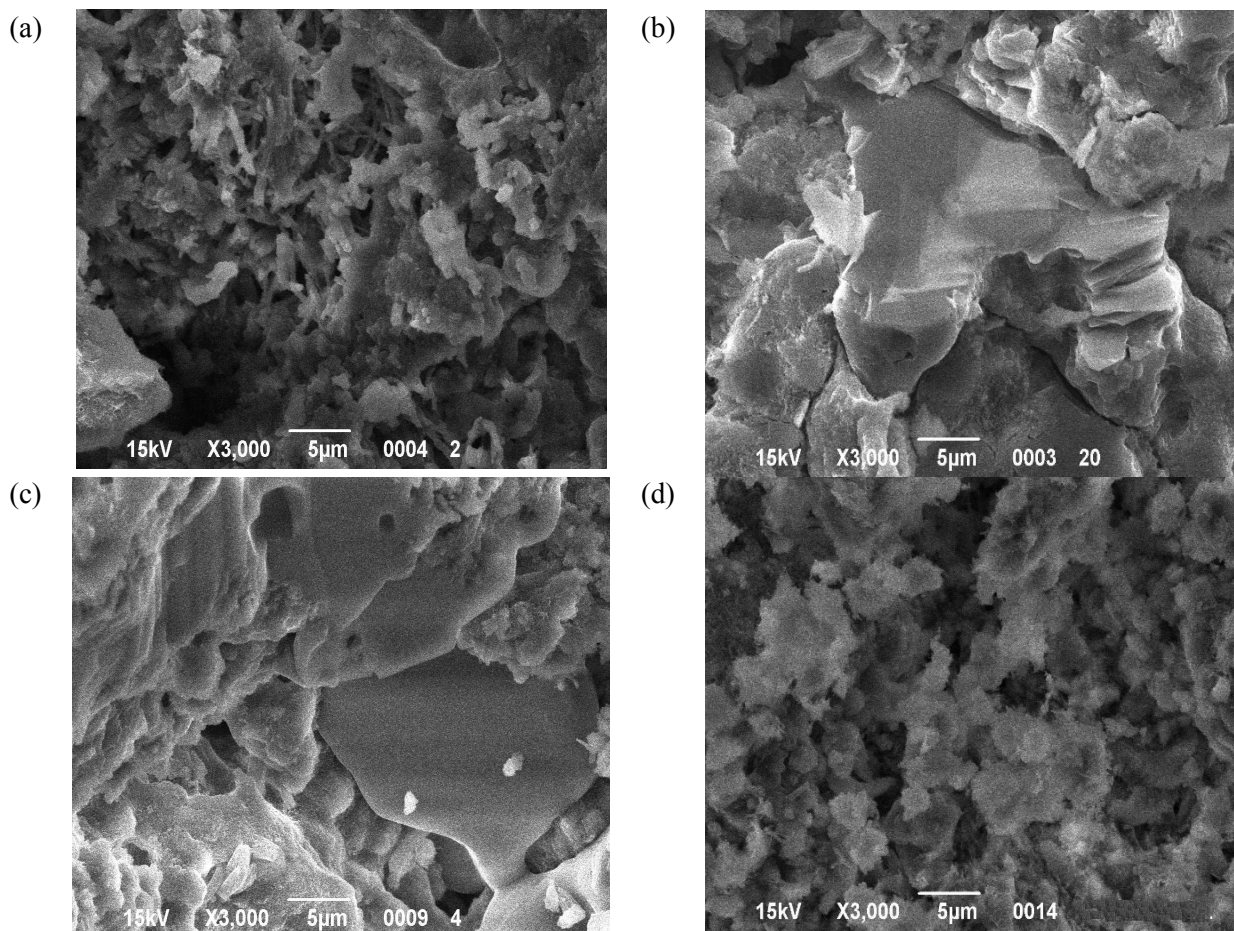


Figure 1. Microstructure of the cement stone modified with highly-dispersed chalk 10 % (a), 20 % (b), 30 % (c), 40 % (d), magnification of $\times 3000$.

The particle size of highly-dispersed chalk can be compared to that of the capillaries of cement stone therefore their addition contributes to the formation of a denser structure. An optimal package of matrix particles is formed at the microlevel in the layers between the structure formation elements; carbonate particles that are poorly soluble in water fill the interlayers between the cement particles and the fine filler particles increasing thus the concrete density and decreasing the concrete penetrability. The volume of capillary pores is usually not exceeding 40 % therefore a total volume of the cementing agent can be increased at least by 40 % due to the addition of highly-dispersed chalk to fill them.

An increase in the porosity of concrete structure containing 40 % of chalk can be explained by the origination of unstable hydrates of a $4\text{CaOAl}_2\text{O}_3\times 13\text{H}_2\text{O}$ (C_4AH_{13}) and $2\text{CaOAl}_2\text{O}_3\times 6\text{H}_2\text{O}$ (C_2AH_6) type with calcium–oxygen ionic bonds that results in degraded strength indices.

The papers [8, 10] give the research data related to the influence of added highly-dispersed chalk on the physical and mechanical properties of concrete. The experiments showed that the addition of highly-dispersed chalk in the amount of 10 % of the cement mass provides an increase in the compression strength of concrete by 3.5 %, bending strength by 11.4 %, water resistance by 20 %, frost-resistance in water by 26 % and in the NaCl solution by 28 %.

The conducted research [11] showed that the addition of highly-dispersed chalk results in an increased concrete strength in corrosive environment. It was proved experimentally that the addition of 10 to 20 % of highly-dispersed organogenic calcite, i.e. chalk results in a considerable increase of the corrosion resistance of concrete in corrosive environment, in particular by 18 % in chloride solutions, by 32 % in sulfate solutions and by 39 % in magnesia solutions.

4. Conclusion

An efficiency of the additive is defined by the consolidation of the microstructure of cement stone due to the distribution of additive grains in the intergranular cement gaps and due to an increase in the dispersion of hydration products for which highly dispersed calcite particles serve as crystallization centers. The research done showed that the presence of highly dispersed calcite (chalk) in the composition of cement stone changes the phase composition of new hydrate formations. The use of highly dispersed calcite results in a decreased content of free calcium hydroxide and in the binding of aluminat phase forming stable hydration products. It contributes to an increase in the corrosion resistance of cement stone when exposed to the action of corrosive solutions.

The experiments showed that 10 to 20 % addition of highly dispersed calcite results in a decreased porosity and improved physical and mechanical properties of concrete in particular frost resistance and corrosion resistance in corrosive environment.

The concretes modified by the addition of highly-dispersed chalk are recommended for the structures exposed to the action of sea water, corrosive groundwater and industrial wastewater containing chlorides, sulfates and magnesium ions.

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