On Standard Requirements to Cement for Concrete Used in Marine Environment

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Abstract. The article describes the process of leaching (washing-out of calcium hydroxide from the cement stone) the concrete in a zone of variable sea level under the action of capillary forces, resulting to increase the diffusion permeability of concrete against aggressive ions. It was noted that along with physical factors like the density (permeability) of concrete, the corrosion processes in the marine environment are associated with chemical factors, in particular with the content of tricalcium silicate in clinker which is the main supplier of calcium hydroxide. In this regard, we researched the current regulatory documents (GOSTs) on cements for the requirements for the maximum content of tricalcium silicate in clinker. The research pointed out the absence of requirements for this indicator there, while many researchers believed that the role of tricalcium silicate was important enough in ensuring the frost and corrosion resistance of concrete in the marine environment in the zone of variable level.

1. Introduction
Density, frost resistance and corrosion resistance are among the main parameters that determine the durability of concretes used in the marine environment in the area of variable water level.

As per the classification of V.M. Moskvin [1], the corrosion of concrete in the marine environment can be of three types. Corrosion type 1 is defined as the process of removal of calcium hydroxide from concrete, that is, “leaching”. Corrosion type 2 is associated with exchange reactions between the components of the cement stone and solutions of magnesium salts. Corrosion type 3 (sulfate) is determined by the accumulation of salts in the pores and capillaries of the cement stone with their subsequent crystallization and an increase in the volume of the solid phase. Corrosion processes in concrete run in parallel to each other and compete with each other. Corrosion destruction of cement stone in all three types of corrosion, including the frost one, occurs with the direct participation of calcium hydroxide $\text{Ca(OH)}_2$ and aluminoferrites.

Sea water is a complex environment containing aggressive to cement stone electrolyte salts including calcium sulfate, magnesium chloride and magnesium sulfate, and sodium chloride. In this connection, the effect of seawater on concrete is defined as the action of chloride-sulfate-sodium-magnesia complex with the following degree of diffusion permeability of ions in descending order: $\text{Cl}^- \rightarrow \text{Mg}^{2+} \rightarrow \text{SO}_4^{2-}$. 
The destructive effect of seawater on concrete consists of physical (alternation of watering and drying, capillary suction, freezing and thawing) and chemical (reaction of sea water salts with hydrated newgrowths of cement) interactions.

The chemical effect of seawater on concrete (in a variable level zone) is mainly due to the presence of NaCl, MgCl\(_2\) and MgSO\(_4\). The reactions of these salts with cement (mainly with Ca(OH)\(_2\)) produce brucite, Friedel salt, and delayed ettringite formation. In the presence of dissolved forms of carbon dioxide, the formation of hydrocarbonate forms is likely.

The presence of chlorides in seawater accelerates the leaching of Ca(OH)\(_2\), CaCO\(_3\) and alumoferrite compounds.

2. Significance of the research

Our studies showed that the cement stone based on high-alite portland cement with w/c = 0.3 has changed in a year of hardening in seawater (starting from 30 days) as follows: the content of Ca(OH)\(_2\) decreased from 10% to 4.8%, while Mg(OH)\(_2\) and Friedel salt, which were initially absent, appeared in an amount of \(~3\%\). The ratio of Ca(OH)\(_2\) to Mg(OH)\(_2\) in the observation period was 46% to 70%, and by the end of the year corresponded to the ratio of their molecular masses \([1-12]\).

Salt corrosion products in the form of crystals on the surface of concrete and on the bottom of the desiccator were studied with the thermogravimetric analysis (TGA). They showed similar brucite-salt triplet compositions of the phases with a significant difference in the content of CaCO\(_3\) and the presence of the amorphous phase 2θ = 22º.

For this reason, for more than a century, one of the tasks of technologists is to reduce the content of free calcium hydroxide Ca(OH)\(_2\) in the concrete, mainly due to the reduction of C\(_3\)S and C\(_3\)A in clinker without “leaning” by active mineral additives.

Many national (Moskvin, V.M., Batrakov, V.G., Kind, V.V., Moshchansky, N.A. and others) and foreign researchers (Lee, F.M., Taylor, H.F., Blanks, R.) emphasized in their works the possibility of the content of C\(_3\)A of up to 5% and more with guaranteed density of concrete and using powerful chemisorption (according to CaO) mineral additives of amorphous modification of silica fume type (CSF) \([14]\) and “Geosil” \([13-15]\).

The value of the concrete density in ensuring its corrosion resistance is reflected in SP 28.133330.2017 “Anticorrosion protection of building structures.”

For example, Table B3 of the Code Specification states that the index of the liquid aggressiveness for these concretes increases by 30-50%, when the concrete watertightness grade changes from W4 to W6 - W8. In other words, the concretes of grades W6 - W8 can resist aggressive liquid with a higher (by 30-50%) content of corrosive ions than concretes of grade W4.

Switching from W4 to W10-W12 increases the liquid aggressiveness index twofold and more. Exposure of complex salt solutions on concrete increases the liquid aggressiveness rate by 20-40%, respectively, when switching from W4 to W10- W12.

As for the concrete structures located in the area of variable sea level, there is a suction under the capillary forces with a variable water motion in the concretes of any density. As a result, calcium hydroxide, including the hydrolysis of minerals, that ensure the strength of cement stone, is being removed from concrete. And the processes of leaching of concrete are more intense at low temperatures, because the solubility of calcium hydroxide increases with a decrease in temperature.

In turn, an increase in the solubility of calcium hydroxide \([2]\) leads to an increase in the diffusion permeability of concrete by an order of magnitude in relation to aggressive ions. Moreover, chlorides are particularly sensitive to the increase in the pH of the liquid phase associated with an increase in the solubility of calcium hydroxide.

Thus, along with the physical factors (permeability of concrete), the corrosion processes in cement stone are largely determined by the mineralogical composition of cement, in particular, by the content of tricalcium silicate, which is the main supplier of unstable in water and air calcium hydroxide. Thus, the corrosion resistance of concretes is provided not only due to low permeability, but also to the
choice of appropriate cements: sulfate-resistant and standardized composition including the use of active mineral additives that bind free calcium hydroxide to compounds of low solubility.

3. Conclusion
The analysis of the requirements for the mineralogical composition of clinker given at the current updated GOST 22266-2013 “Sulfate-resistant cements. Technical conditions” showed that this standard has no requirement for limiting the content of tricalcium silicate, while the previous GOST 22266-94 regulated the content of C₃S by a limit of 50%.

At the same time, the updated GOST has tightened the requirements for the content of tricalcium aluminate C₃A in the clinker from 5% to 3.5% for the cements without mineral additives.

The requirements for C₃A content in the mineral-added cements remained unchanged at 5% or less. GOST R 55224-2012 “Cements for Transport Construction” limits the maximum content of tricalcium aluminate by 7%, and tricalcium silicate (C₃S) by 55% and more.

Thus, the analysis of the current standards showed that the GOSTs for cement have no requirements for limiting the content of tricalcium silicate, which, in our opinion, to a certain extent contradicts the former (classical) idea about ensuring corrosion resistance and frost resistance of concrete in the marine environment.

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