Properties of the phase components of the modified cement system

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Summary: The article presents the results of the study of the influence of modification on the clinker mono minerals structure formation. A research of synthesized and modified mineral systems resistance to the weathering (carbonation, varying conditions), as well as to the aggressive solutions exposure was conducted.

Keywords: cement system, modification, mono minerals, resistance.

INTRODUCTION

There are many ways of purposeful control of structure formation of the concrete mixtures’ cement systems at different stages of hardening [1, 3, 6]. The most rational way is a structure adjustment through the introduction of modifiers. Modification of cement systems by various chemically-active components intentionally changes hardening and structure formation processes, provides the improvement of the technological properties of the material [2, 4, 7-9]. However, modification has an ambiguous impact on the properties of mono minerals of the cement system [12, 13, 21, 22, 26].

Modification means creation of favorable conditions for the clinker minerals chemical interaction and further formation of the concrete cement matrix with specified properties. The simplest way of intensification of hydration process and optimization of cement systems structure formation is a usage of polyfunctional admixtures [5, 11, 16, 19, 23]. Such additives, intensifying hydration process, having an effect on the hydration products morphology and their structure formation process, can’t be composed of one component [15, 27, 28, 30]. Obviously, such additives must form a complex with polyfunctional properties. At the same time, organic plasticizers, widely used at building industry enterprises, require an addition with special mineral components, chemically interacting with clinker minerals. Thus, it’s necessary to choose a complex composition modifier with polyfunctional effect on the structuring cement system. An optimizing effect of the complex modifier becomes apparent on the crystallochemical level of structure formation. Consequently, crystallochemical optimization of the cement systems structure formation may be performed by a special complex, based on modern non-deficit and effective components [10, 17, 18].

Nowadays there are many ways of modification of binding systems, most of them based on the turbulent mixing of components. At the turbulent motion material particles
move randomly both in the direction of current and transversely to it. The particles interpenetrate from one layer to another, the number of their encounters increase [14, 19, 20, 24].

Usually abroad turbulent mixing is used for the preparation of injection compositions, as they help to raise the stability of concrete mixtures.

In the authors’ opinion, turbulent mixing leads to the deflocculation of a cement-water suspension, as a result saturation of suspension with colloid particles increase, the paste becomes more stable, bleeding reduces. As a result of turbulent mixing, cement paste viscosity decreases to a certain point in time, when the mixture temperature rise due to the exothermal reaction of clinker minerals hydration starts acting back and the mixture thickens. The optimal duration of mixing, when paste viscosity decreases with the simultaneous reduce of bleeding, is in a certain relationship to a water-cement ratio [10, 17, 18, 25].

The authors [18, 23] are of opinion that turbulent treatment leads to an increase of the cement specific surface area due to the grinding of fine fraction. However, the results of the research conducted by authors [10, 29, 30] showed that specific surface area remains unchanged. Hence, contradictoriness of opinions is indicative of insufficient knowledge of binding systems modification. An ambiguous impact of different modifiers on clinker mono minerals should also be taken into account, as in bulk this may have a negative impact on the processes of structure formation of the concrete cement matrix.

PURPOSE

The purpose of the work is a research of synthesized and modified mineral systems resistance to the weathering (carbonation, varying conditions), as well as to the aggressive solutions exposure.

RESEARCH DATA

Study of the property change of the phase components of the modified cement system during six months carbonation shows that the bending strength of both, hydrated calcium silicate (tobermorite group) and xonotlite, diminishes, whereas on the contrary the strength of the highly basic hydrated calcium silicate significantly increases (Table 1). In this conditions low-basic hydrosilicates, especially tobermorite group, despite their higher density, carbonate much faster and change more intensively in comparison with the less dense highly basic hydrated calcium silicate.

Table 1. Operating abilities of modified monomineral systems

<table>
<thead>
<tr>
<th>Phase components</th>
<th>Bending resistance, MPa</th>
<th>Freeze-thaw resistance, cycles</th>
<th>Degree of shrinkage after carbonation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>after synthesis</td>
<td>after carbonation</td>
<td>after alternate wetting and drying</td>
</tr>
<tr>
<td>C–S–H(I)</td>
<td>8,0</td>
<td>9,3</td>
<td>8,6</td>
</tr>
<tr>
<td>Xonotlite</td>
<td>14,3</td>
<td>11,6</td>
<td>10,2</td>
</tr>
<tr>
<td>C₂SH(A)</td>
<td>4,5</td>
<td>5,9</td>
<td>6,6</td>
</tr>
<tr>
<td>C₂SH(C)</td>
<td>2,8</td>
<td>6,2</td>
<td>5,4</td>
</tr>
<tr>
<td>C₃AH₆</td>
<td>4,4</td>
<td>6,2</td>
<td>5,6</td>
</tr>
</tbody>
</table>

The reason of it is a big specific surface area of C–S–H(I), which accelerates its interaction with carbonic acid gas and leads to a fast oversaturation and occurrence of a big number of nuclei. A lot of small defective crystals emerge as a result. Besides, the significant carbonation speed of low-basic hydrated calcium silicate (tobermorite group) can be explained by its layer structure.

Access of moisture-dissolved carbon acid gas inside the hydrated calcium silicate...
takes place together with hygroscopic water when a water molecule penetrates along the layered crystal cleavage surface. The carbonation speed of hydrated calcium silicate to a great extent depends on the humidity of environment. At the same time, ions of Ca\(^{2+}\) in hydrosilicate, being a center of water molecule persorption according to the two types of a bond (silicon-oxygen radicals and OH ions) in a crystal cell, take carbon acid gas much easier. If CO\(_2\) is replaced according to OH\(^{-}\) bonds, then CaCO\(_3\) forms instead of hydrosilicate, and if the replacement takes place according to the silicon-oxygen radicals bond, then scawtite forms. It should be mentioned that in the usual terms replacement of CO\(_2\) takes place according to the ionic bond OH\(^{-}\).

It is established that modified concrete strength and deformability change differently depending on the concentration of carbon dioxide in the atmosphere. In the first case, when the concentration of CO\(_2\) is weak, i.e. the oversaturation of the solution is not too big, calcite crystallizes calmly and its crystals are larger. Calcite crystals grow due to the joining of atoms near the active centers, calcite has better structural properties (less defect and dislocation cluster).

In the second case, when the CO\(_2\) concentration is strong and the oversaturation is significant and even exceeds a critical value, calcite crystallization takes place in a spontaneous formation of nuclei, small crystals of the same size form for a certain period of time. Therefore, to improve the structure and properties of the crystals of calcite, which is one of the products of hydrated calcium silicate carbonation, it’s necessary to reduce oversaturation, i.e. to reduce the concentration of the carbonized environment.

The strength of the carbonated calcium hydrosilicate is determined by the degree of crystallization and the size of crystals. In the process of carbonation of a less crystallized C–S–H(I) a large amount of loose calcium carbonate is formed.

A physical phenomenon, accompanied by bulking of a solid phase, and bringing forth the inherent stresses in concrete can be observed in the process of carbonation of calcium hydrosilicate, besides the chemical processes listed above. The intensity of stress and its tension seem to raise with the increase of carbonation speed.

Study of changes of the hydrated calcium aluminate and calcium hydrogarnet properties showed that when artificially carbonated the hydrated calcium aluminate strength increases in a greater degree than calcium hydrogarnet strength. Judging by the amount of the combined CO\(_2\) this corresponds to a significant degree of carbonation of hydrated calcium aluminate in comparison with calcium hydrogarnet. In the conditions of alternate wetting and drying during 50 cycles the strength of tobermorite group and xonotlite decreases and the strength of C\(_2\)SH(A) and C\(_2\)SH(C) increases, but in a lesser degree than at carbonation (Table 1). In these conditions the strength of hydrated calcium aluminate almost doesn’t change and the strength of calcium hydrogarnet increases slightly. Along with this an imperceptible shrinkage is observed.

The layered structure and water contained in the structure of hydrated calcium silicate (tobermorite group) are able to change depending on the effect of environment. If we consider a layered crystal of tobermorite as compiled packages connected along the basal planes of the elementary crystallites than abrupt change of desorption curves is due to exudation of hygroscopic water from the interplanar spacing. At the same time a unit cell \(c\) parameter changes from 27 to 24.6 \(10^{-10}\) m [5, 12, 15].

Properties of hygroscopic water in hydrated calcium silicate with layered structure depend on H\(_2\)O/SiO\(_2\) ratio. When the ratio value is less than one then molecules of hygroscopic water are not included in the structure of the crystal lattice and have a mobility of liquid water and so the water is inconstant due to the environment factors variations [6, 22].

It is established that when silica-containing component is introduced in the amount more than 20% of cement weight then new phases form, and if the amount is less the
20% then there is a replacement of ions in the crystal lattice of the cement phase components. The ability of the cement phase components to replace isomorphously the ions of other elements in their lattices varies according to the type of a mineral modifier, the similarity of its physical and chemical characteristics and atomic size with the cement phase components. We have studied the processes of substitution of ions of Na$^+$, Al$^{3+}$, Fe$^{3+}$, SO$_4^{2-}$ and CO$_3^{2-}$ by the hydrated calcium silicate and the change of the properties of the latter during carbonation. It is established that the optimal amount of mineral modifier, by the degree of substitution and its positive influence on the properties of hydrated calcium silicate, varies depending on the ratio CaO/SiO$_2$ in the mixture and intensity of modification.

The positive effect of substitution of these ions on the properties of the cement phase components can be estimated to a large extent by the degree of shrinkage behavior after carbonation of the hydrated calcium silicate. It is established that that the major part of the shrinkage of C–S–H(I) takes place on the first 5…10 days, shrinkage of the tobermorite on the 20…25 days, xonotlite and C$_2$SH(C) on the 10…20 days. Depending on the type of modifier shrinkage processes of the hydrated calcium silicate proceed in varying degrees. So, for example, replacement of Na$^+$ reduces shrinkage of C–S–H(I) up to 4 times, tobermorite and C$_2$SH(C) almost up to 1,5 times. In these conditions replacement of ions of Al$^{3+}$ reduces the shrinkage of C–S–H(I) and tobermorite up by 10…20%, xonotlite up to 1,5 times, C$_2$SH(C) up to more than 2,5 times. Replacement of CO$_3^{2-}$ and SO$_4^{2-}$ is conductive to the significant reduction of shrinkage, especially in tobermorite and xonotlite – up to 2 times, in C$_2$SH(C) almost up to 1,5 times.

Analysis of the data shows that selection of the type and the degree of substitution of ions allows reducing the shrinkage of hydrated calcium silicate extensively. Especially it refers to hydrated calcium silicate C–S–H(I) and tobermorite, which have a significant shrinkage, their shrinkage can be brought to the level of low-shrinkage type of hydrated calcium silicate, such as xonotlite and C$_2$SH(C). Although the shrinkage of the latter is high, however it can be minimized by substituting ions of Al$^{3+}$, Fe$^{3+}$ and SO$_4^{2-}$ in their lattice. Beneficial effects are caused by the fact that ions of Al$^{3+}$, Fe$^{3+}$, SO$_4^{2-}$ are in the structure of hydrated calcium silicate, substituting Si$^{4+}$, and Fe$^{3+}$ hardly gets in the crystal structure due to the large ionic radius in comparison with Si$^{4+}$ [27]. The replacement of Fe$^{3+}$ has a more beneficial effect on the shrinkage of xonotlite and C$_2$SH(C) which are synthesized at higher ratio of CaO/SiO$_2$, than C–S–H(I).

The study of the corrosion stability of the phase components of the modified cement system in sulphate solutions within 12 months showed that the most intensive fracture of hydrated calcium silicate can be observed in MgSO$_4$ solutions. In this solution in the initial period of storage (up to 3 months) the strength of the samples increases, in the sequel it reduces. The strength in Na$_2$SO$_4$ solution starts reducing from the initial period of storage. Low-basic hydrated calcium silicate (tobermorite group and xonotlite) corrode more in the sulphate of magnesia solutions, than highly basic hydrated calcium silicate [C$_2$SH(A) и C$_2$SH(C)]. After one year storage in a 2.5% solution of MgSO$_4$ their resistance coefficient decreases to 0,76…0,68.

The increased corrosive action of MgSO$_4$ solutions on hydrated calcium silicate in comparison with Na$_2$SO$_4$ solutions is due to the fact that ions of the latter because of the heterovalent substitution by the scheme 2Na$^+$ ↔ Ca$^{2+}$, as well as the difference in their ionic radii complicate their interaction, while the substitution Mg$^{2+}$ ↔ Ca$^{2+}$ between cations Mg$^{2+}$ and Ca$^{2+}$, which have closer ionic radii, goes on faster. Reactive capacity of the specified solutions with hydrated calcium silicate is also determined by the adsorption capacity of their ions. So, polyvalent cations of Mg$^{2+}$ are better adsorbed in hydrated calcium silicate than monovalent cations of Na$^+$. This can be explained by Pyeskov-Fajans rule: when hydrated calcium silicate interreacts with MgSO$_4$ solution, all the occurring products (MgSO$_4$ and gypsum) are hardly soluble,
whereas with Na$_2$SO$_4$ solution only gypsum is hardly soluble and the second type of the reaction product NaOH is in the liquid phase. Furthermore, in these conditions adsorbability of the cations of Mg$^{2+}$, which form with OH$^-$ ions less soluble Mg(OH)$_2$ (water solubility at 20°C makes 0.9 mg/l), is more than adsorbability of SO$_4^{2-}$ ions, which form gypsum with cations of Ca$^{2+}$ (its water solubility makes 2.41 mg/l).

From this it follows that a double electric layer is formed on the border of hydrated calcium silicate and the specified solutions, and in MgSO$_4$ solution a double electric layer on the surface of hydrated calcium silicate is formed from the ions of Mg$^{2+}$ and OH$^-$, and in Na$_2$SO$_4$ solution from the ions of Ca$^{2+}$ and SO$_4^{2-}$. The speed of the electric double layer formation depends on the adsorption capacity of the ions of solutions, and this determines the intensity of the corrosive processes.

Considering the kinetics of cement phase components interaction with aggressive solutions it may be said that chemical heterogeneous reaction rate is determined by the interacting particles diffusion rate. As a result of interaction of the hydrated components of cement with the corrosive environment an interfacial film occurs, it has different density depending on the ratio of a volume of reaction products and reacting substances. This film, consisting of a mixture of CaSO$_4$·2H$_2$O, Mg(OH)$_2$ and gel SiO$_2$, inhibits or in some cases neutralizes the rate of heterogeneous reaction between the binding material and liquid corrosive environments if the condition of continuity according to the rule of Pming and Betwarts is satisfied [10]. According to this rule the molecular volume of the mixture of CaSO$_4$·2H$_2$O, Mg(OH)$_2$ and gel SiO$_2$ must be more than the volume of binding materials spent on the formation of the molecules of these compounds. Otherwise, the film created by the molecules of these corrosion products is not enough to cover with the solid layer the entire surface of binding materials, as a result it is loose and porous. Consequently, protective properties of the film depend on its quality (density and continuity), i.e. on the diffusion coefficient of the particles interacting through the film.

The analysis showed that interfacial films formed at the interaction of C$_2$SH(A) and C$_2$SH(C) with sulphate solutions (Na$_2$SO$_4$ and MgSO$_4$) have a dense structure and when tobermorite group and xonotlite interact with the specified solutions they, on the contrary, have a porous structure. It means that ions of xonotlite, tobermorite, C–S–H (I) and interacting solutions can freely diffuse through them.

Thus, the formation of a porous film in the 2.5% solution of MgSO$_4$ is one of the reason of such a fast fracture of low-basic hydrated calcium silicate. But, despite this they fracture more slowly in a 5% solution of Na$_2$SO$_4$ that is the consequence of the less reacting capacity of the ions of Na$^+$, than of Mg$^{2+}$.

CONCLUSIONS

1. Based on the above we can conclude that highly basic hydrated calcium silicate in solutions of MgSO$_4$ and Na$_2$SO$_4$ must fracture slower or slightly lose its original strength due to the protective film. In fact, in MgSO$_4$ solution that's the way it is and in Na$_2$SO$_4$ solution, on the contrary, highly basic hydrated calcium silicate fractures intensively.

2. Such inconsistency of the mechanism of Na$_2$SO$_4$ solution on the highly basic hydrated calcium silicate is due to the fact that the resulting corrosion products are reactive to each other.

3. So, the presence of NaOH in the liquid medium complicates the formation of gypsum crystals and their intergrowth with each other and dissolving in it, they form porous, available for ionic diffusion interacting particles. Besides, sodium hydroxide partially transfers SiO$_2$ gel into soluble sodium silicate. This allows generating a protective film whose volume is larger than the raw
REFERENCES


СВОЙСТВА ФАЗОВЫХ СОСТАВЛЮЩИХ МОДИФИЦИРОВАННОЙ ЦЕМЕНТНОЙ СИСТЕМЫ

Дмитрий Руденко

Аннотация. В статье представлены результаты исследований влияния модификации на структурообразование мономинералов клинкера. Исследована стойкость синтезированных и модифицированных мономинеральных систем к воздействию атмосферных факторов (карбонизации, переменных условий), а также агрессивных растворов. Ключевые слова: цементная система, модификация, мономинералы, стойкость.