Study of the Hydrosilicate Phases Formation Process of Portland Cement with Disaccharide Additives

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Abstract. The article is devoted to the study of the cement stone hydrate phases formation in the presence of significant amounts (2%) of isomeric disaccharides - sucrose, maltose and lactose. Attention to disaccharides as modifying agents of cement stone is due to their ability to influence the ratio of high and low density cement gels in the composition of cement stone. To implement Portland cement hydration process in the presence of significant amounts of disaccharides cement grinding in the presence of carbohydrate solutions was used. It was found that the molecular structure of carbohydrate does not affect the elemental and phase composition of hydration products. Hydrosilicates in the presence of carbohydrates and aside of the molecular structure of the latter form the phases of the cryptocrystalline structure. The formation of cryptocrystalline phases is accompanied by occlusion of disaccharides; the residual content of disaccharides in the liquid phase of suspensions does not exceed 0.3% of the initial amount of modifying carbohydrate.

1. Introduction
Since the publication of papers on the structural features of the cement gel [1,2], interest in carbohydrates has increased significantly. This tendency is determined by several reasons: on the one hand, polysaccharides and saccharose, as the most accessible and studied carbohydrate, exhibit the properties of an effective set retarder, and its overcoming is marked by acceleration of hydration processes and full restoration of the strength characteristics of cement stone [3,4,5]. On the other hand, the amount of low density cement gel increase in the presence of saccharose [6] indicates the ability of saccharose to influence the processes of cement gel formation at the level of differentiation of its nanostructure [7,8]. Determining the mechanism of this influence is able to open the managing the physicomechanical properties of a cement gel at the nanolevel, which is the most promising approach to controlling the properties of cement stone [9,10]. However, the interaction of carbohydrates with hydrated phases of cement stone has a very wide range of impacts. For instance, the adsorption of monosaccharides affects the phase formation of ettringite and the nature of complexation with calcium ions depending on their stereochemistry [11], the adsorption of sucrose affects the cement clinker individual minerals reactivity [12,13] and contributes to the formation of mechanically strong polymolecular adsorption layers according to the scheme: Saccharose - Ca²⁺ - Saccharose [14]. The situation is further complicated by the fact that the dosages of carbohydrates and, in particular, saccharose used in the practice of building materials science are quite small (for saccharose - no more than 0.3%) [15,16], and therefore the formation of significant amounts of carbohydrate-mineral
adducts that could affect the properties of the cement stone are generally not observed. In the presence of large amounts of saccharose (1% or more), the hydration processes of cement clinker silicates are almost completely suppressed [13], as a result, the accumulation of significant amounts of carbohydrate-hydrosilicate adducts is also impossible under normal hydration conditions. Thus, the study of disaccharides effect and, in particular, saccharose on the structure formation of calcium silicates as the basis of cement stone is complicated, first of all, by the low rate of hydrolysis of clinker minerals in the presence of carbohydrate. However, according to data [13,14], this inhibition is due only to the specificity of the adsorption interaction of saccharose with a silicate surface, and, therefore, it can be overcome by the method of mechanochemistry, i.e. by carrying out the hydration process under grinding conditions, which can be defined as activated hydration. Information on the structure and composition of the modified hydrate phases of the cement stone will make it possible to understand the nature of the effect of disaccharides on the formation of a low-density cement gel.

Thus, the purpose of this paper is to study the formation of hydrosilicate phases of cement, obtained under grinding conditions in the presence of an aqueous solution of a disaccharide (saccharose, maltose, lactose). The use of isomeric disaccharides will allow to evaluate the differentiation of these carbohydrates according to the structural feature.

2. Materials and methods

Cement type CEM I (CEM I 42.5 N of Holcim (Rus) CM OAO Volsk plant) was used as a binder. High purity agents (99.9%) were used as disaccharides.

Grinding suspension - A solution of carbohydrate (W/C = 2) was carried out in a planetary mill for 1.5 hours. To prepare a solution of carbohydrate, the latter was taken in an amount of 2% by weight of cement. The aqueous phase of the resulting suspension (filtrate) was separated and subjected to quantitative analysis for the presence of residual amounts of modifying disaccharide colorimetric method (table 1); the solid phase was dried at a residual pressure of 0.2-0.3 kPa/cm² and a temperature of 40-50°C and subjected to elemental analysis by the method of EDS-spectroscopy (table 2).

The carbohydrate content was determined by a colorimetric method using a phenol-sulfate reaction with a Multiscan Ascent micrometer photometer in a microplate format (ThermoLabsystems, Finland). 50 μl of the test solution is pre-applied to the wells of the polystyrene plate. Calibration solutions are prepared in advance (solutions with a given concentration of glucose). Next, 50 μl of 5% phenol and 250 μl of concentrated sulfuric acid are added to all wells. After five minutes of incubation at room temperature, the concentration of carbohydrates in the test and calibration samples was measured. The principle of the method is based on transferring the determined sugars to furfural compounds under the action of concentrated sulfuric acid, which differ in extinction at 490 nm depending on their concentration, glucose solutions with a known concentration were used for calibration, the standard deviation did not exceed 5%.

| Modifying carbohydrate | Saccharose | Lactose | Maltose |
|------------------------|------------|---------|---------|
| Carbohydrate content in filtrate (mkg/ml) | 9.42 | 2.75 | 1.84 |
| The residual carbohydrate content of the mass used to modify the carbohydrate (%) | 0.312 | 0.091 | 0.061 |

Structural studies of nanoparticles were monitored using a CarlZeiss Libra 120 transmission electron microscope (TEM) equipped with a accessory for SAED analysis.

The elemental composition of the products of mechanochemical synthesis was determined using a scanning electron microscope with a JEOL JSM 7001FA field cathode equipped with an EDS accessory.

Changes in the phase composition of the modified cement stone were recorded using an ARLX’tra x-ray diffractometer. Structural changes tenuously crystallized phases were determined by X-ray diffractometer during the shooting: Kα-Cu, anode current of 25 mA, voltage 25 kV, burst rate of 2
degree/min, Kα-Cu, anode current of 30 mA, voltage 40 kV, burst rate of 2 degree/min, the width of the optical gap of 4 mm.

Table 2. The elemental composition of modified cement hydration products samples.

| Element   | By wt (%) | Atom (%) | Element   | By wt (%) | Atom (%) |
|-----------|-----------|----------|-----------|-----------|----------|
| Lactose   |           |          | Si        | 13.14     | 9.87     |
| C         | 2.84      | 5.00     | Si        | 12.77     | 9.77     |
| O         | 50.39     | 66.47    | Ca        | 25.90     | 13.64    |
| Al        | 2.19      | 1.71     | Fe        | 2.23      | 0.84     |
| Saccharose|           |          | Si        | 12.77     | 9.77     |
| C         | 3.19      | 5.71     | Si        | 12.04     | 9.24     |
| O         | 47.90     | 64.35    | Ca        | 28.35     | 15.20    |
| Al        | 2.03      | 1.62     | Fe        | 2.62      | 1.01     |
| Maltose   |           |          | Si        | 12.04     | 9.24     |
| C         | 2.95      | 5.30     | Si        | 12.04     | 9.24     |
| O         | 48.25     | 65.05    | Ca        | 31.37     | 16.88    |
| Al        | 1.51      | 1.21     | Fe        | 1.84      | 0.71     |
| Control composition | |          | Si        | 13.47     | 10.30    |
| C         | 2.35      | 4.20     | Si        | 13.47     | 10.30    |
| O         | 48.99     | 65.76    | Ca        | 27.63     | 14.81    |
| Al        | 2.17      | 1.73     | Fe        | 2.30      | 0.88     |

3. Results and discussion

The residual content of modifying carbohydrates did not exceed 0.4% of carbohydrate mass used for the modification, which corresponds to almost quantitative absorption of carbohydrates by activated hydration products. It should be noted that maltose and lactose are more effectively absorbed by the hydrated phases of the cement stone than saccharose - the difference in the residual carbohydrate content is 3 times more. Thus, the structure of the modifying carbohydrate determines the level of occlusion of the latter by hydrated phases of the cement stone.

Analysis of cement modified hydroxysilicates samples elemental composition (table 2) allows us to estimate the composition of the modified hydrate phases. It is necessary to take into account the effect of the samples surface carbonization, as a result of which, according to the composition of the control sample, 2.35% of carbon and 6.26% of oxygen are introduced into the system. According to this, the composition of cement hydroxysilicates modified with lactose can be expressed by the gross formula:10SiO$_2$·14CaO·19H$_2$O; in case of modifying with sucrose - 10SiO$_2$·15CaO·16H$_2$O; in case of modification with maltose - 10SiO$_2$·17CaO·19H$_2$O. The composition of the hydration phases of the control sample is described by the formula 10SiO$_2$·15CaO·18H$_2$O. Elemental analysis demonstrates a relatively high degree of the modified hydroxysilicate compositions identity to the control composition. Minor fluctuations in the calculated content of CaO and H$_2$O (within 13%) can be attributed to the errors of the experiment, as the weighted average composition of the sample surface layer is estimated, and therefore, the influence of inclusions of non-hydrated cement clinker (figure 1), which is separated from the reaction no mass was produced. The data presented on the elemental composition of modified cement samples hydration products indicate that carbohydrates do not significantly affect the hydration process of clinker minerals - in all cases hydrate phases are formed, their composition is determined by the composition of the initial mixture.
Phase analysis of mechanochemical synthesis products showed that in the presence of all considered modifying carbohydrates the main phases in the composition of hydration products are: C3S (alit), 3CaO·Fe2O3·3CaSO4·31-35H2O (ferrous ettringite), Ca(OH)2 (portlandite), weakly crystallized phases (2ϴ = 20-40 degrees), the presence of aluminates is possible, in particular, in the form of 3CaO·Al2O3·6H2O (figure 1). The analysis of portland cement modified hydrate phases diffractograms allows to draw several conclusions. First, the presence of Portlandite signal on diffractograms, which is usually not seen during cement hydration in the presence of carbohydrates under normal conditions, is apparently due to the absorption of carbohydrates by hydration phases, so that Ca(OH)2 can form a crystalline phase. Secondly, the high degree of mutual identity of samples modified with different disaccharides phase composition suggests that the structure formation of the hydrated phases of the cement stone in the presence of disaccharides does not depend on the nature of the modifying carbohydrate.

The high content of glandular ettringit is a consequence, on the one hand, of the grinding bodies cupping, and on the other hand, of the presence of carbohydrates stabilizing the ettringite phases [17]. Under these conditions, the question arises as to whether prismatic particles present in microelectronic photographs belong to ettringite phases. To solve this issue, the SAED method was used - an electron diffraction mode from a dedicated site. The advantage of this method is the high locality of the

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**Figure 1.** Diffractograms of modified cement stone samples, obtained in the conditions of wet grinding and dried at 25°C. Modifiers: (a) – lactose, (b) – maltose, (c) – saccharose, T – ettringite, P – portlandite, A – alit, B – γ bleaches; possible presence L - 3CaO·Al2O3·6H2O.
analysis, i.e. the possibility of obtaining a diffractogram, in our case, from a single nanoobject (figure 2).

![Figure 2](image1.jpg)

**Figure 2.** The results of the SAED analysis of Portland cement hydration products in the conditions of wet grinding, modified: a - sucrose, b - maltose, c - lactose. In the upper part of the figure prismatic particles are analyzed, in the lower part there are corresponding electron-diffraction patterns.

The results of the SAED analysis clearly demonstrate that the prismatic particles that are massively formed during hydration of the modified portland cement under grinding conditions, aside of the type of modifying carbohydrate, are a cryptocrystalline body, and therefore do not belong to the ettringite phases and are modified hydrosilicates. Thus, the study of the composition and structure of cement hydration products modified with isomeric disaccharides leads to the following conclusions:

- Disaccharides do not have a significant effect on the nature of clinker minerals activated hydration. The composition of the hydration products formed is determined by the composition of the initial mixture. The molecular structure of the modifying disaccharide determines the level of carbohydrate occlusion by the mineral matrix.
- The phase composition of the modified hydration products does not depend on the type of modifying carbohydrate and is represented by the phases of cement clinker, hydroaluminates, portlandite, ettringite and slightly crystallized phases.
- Hydration products formed during the activated hydration of cement, aside of the molecular structure of the modifying disaccharide present, form the phases of cryptocrystalline structure.
- Modified cement hydration products actively absorb carbohydrates from solution. The carbohydrates present in the hydration phases prevent their recrystallization and stabilize the particles of the hydration phases obtained during activated hydration. The occlusion of carbohydrates by the hydrated phases of the cement stone, apparently, is the main reason for the increase in the content of the cement gel of low density, because the presence of carbohydrate molecules in hydrosilicates prevents their compaction.
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