Modification of cement systems with oxalic aldehyde

N V Subbotina¹, N P Gorlenko¹, Ju S Sarkisov¹, L B Naumova² and T S Minakova³
¹Tomsk State University of Architecture and Building, Chemistry Department, Tomsk, 634003, Russia
²National Research Tomsk State University, Analytical Chemistry Department, Tomsk, 634050, Russia
³National Research Tomsk State University, Physical and Colloid Chemistry Department, Tomsk, 634050, Russia
E-mail: subnv@sibmail.com

Abstract. The experimental results of physical-chemical properties of composite materials on the basis of cement and wood waste modified by an aquatic solution of oxalic aldehyde are presented in this paper. The injection of a chemical addition agent being in optimal concentration is shown to result in the increase of compressive strength of a cement stone by 30%, that of wood-cement composition — in 7 times. IR spectroscopy investigations, microphotographs of structures, kinetics of samples strength changes are shown.

1. Introduction
The injection of chemical addition agents in the compositions based on cement is one of the most effective methods to increase building materials operational properties. For example, the injection of oxalic aldehyde having optimal concentration into a concrete mixture allows increasing the compressive strength, regulate the duration of concrete composition setting [1]. Modification of wood with the help of chemical additional agents of organic origin is of great importance now. The usage of low quality technogenic wood raw material as one of the components for the building materials will allow solving not only the problem of industrial wastes utilization but the ecological task dedicated to the environment conservation. During the last decades wood-cement materials such as fibreboard, woodcrete, and wood-chip rafts are becoming widely used in construction. The pace of development of materials production in this branch of industry, however, is limited by quite low factors of operational characteristics, such as compressive strength, water absorption and others [2-5]. One of the most effective methods of increasing the quality of building materials based on wood-cement compositions application is the modification of the system by means of chemical additional agents. Oxalic aldehyde refers to the perspective additional agent while solving the problems of building materials quality improvement due to the manifestation of different properties this compound possesses.

Oxalic aldehyde is a high active non-toxic substance easily undergoing the reactions of oxidation, reduction and polymerization. It possesses the properties of a crosslinking agent that defines its application for polymer cellulose-containing materials production. It is capable for suppressing water and returning it into the volume of composition during the late periods of structure formation that must lead to the increase of hydration degree for the grain of cementing agent. These properties permit to
confirm the fact that oxalic aldehyde is a perspective chemical additional agent in cement compositions especially when the wood is used.

The aim of the paper is to study the processes of structure formation and to determine the physic-chemical properties for composite materials based on cement and wood waste by means of their modification with oxalic aldehyde.

2. Materials and methods

The processes of structure formation of the system “cement - water” at the initial time of hardening was estimated according to the values of setting duration with the help of Vica apparatus GOST 310.3-76, and at the final time after 28 days of hardening in wet conditions the samples sized \((5\times5\times5)\times10^{-2}\) m were studied to clear up the limit of compressive strength. For preparation of wood-cement mixture the pine sawdust or chip was used as a wood aggregate. The mixtures obtained by such methods were prepared in the following way: a wood aggregate was treated with an aquatic solution of oxalic aldehyde having different concentrations and Portland cement was injected in the process of agitation. Then this mixture was placed into forms-blocks sized \((5\times5\times5)\times10^{-2}\) m, and the impaction was carried out. After stripping of the samples the experiments on compressive strength at different time of composition setting were fulfilled. In both cases cement of brand 400 was used.

3. Results and discussion

The experimental data are presented in Table 1 and Figure 1.

Table 1. The values of the limits for compressive strength, the beginning and the end of cement stone samples setting after 28 days of hardening for the system “cement - water” in accordance with the concentration of oxalic aldehyde solution.

| Number of the sample | Concentration of oxalic aldehyde (mass. %) | The beginning of the system “cement – water” aquatic solution setting (min) | The end of the system “cement – water” aquatic solution setting (min) | The limit of compressive strength (MPa) |
|----------------------|------------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|-------------------------------------------|
| Control sample       | 0.00                                     | 210                                                               | 250                                                               | 40.3                                      |
| Sample № 2           | 0.16                                     | 180                                                               | 390                                                               | 5.4                                       |
| Sample № 3           | 0.33                                     | 90                                                                | 360                                                               | 47.0                                      |
| Sample № 4           | 0.67                                     | -                                                                 | -                                                                 | 0                                         |

The results of the experiment show (Table 1) that the compressive strength of modified samples in the system “cement - water” was increased approximately by 30%, the initial setting time of the cement composition was decreased and the final one was increased in comparison with the control samples at the optimal concentration of oxalic aldehyde solution which equals to 0.16 % mass. The effect obtained can be explained with the fact that oxalic aldehydes suppresses water and gradually returns it into the system of structural new compounds during the later setting time that can increase the degree of cement particles hydration and, hence, results in increasing the compressive strength of the samples.

In the system of “wood – cement – water” (WCW) the compressive strength in the final time of structural formation is increased in comparison with control samples by 7 times (Figure 1). In this case the significant dependency of samples strength from the concentration of oxalic aldehyde solution injected into the system is observed. Such essential deviations of samples strength compared with the wood-cement composition without injecting of any chemical additional agent is probably connected with the chemical interactions of oxalic aldehyde with wood. Therefore, for the interpretation of obtained results IR- spectra for wood samples and WCW transmission were made (Figure 2).
Figure 1. Kinetics of the limits for compressive strength changes which were detected for wood-cement composition and a control sample modified by an aquatic solution of oxalic dehyde in comparison with the control sample: a – a control sample, b – WCW tempered by 3% solution of oxalic dehyde, c - WCW tempered by 0.2 solution of oxalic dehyde, d – WCW tempered by 1% solution of oxalic dehyde, e – WCW tempered by 2% solution of oxalic aldehyde.

Figure 2. IR- spectrum of pine wood.
It can be concluded from the analysis of IR-spectra presented in Figure 2 that the line of valence vibration of O-H bond (3200 sm$^{-1}$) is shifted in a high energetic part of the spectrum 3339 sm$^{-1}$ that indicates the appearance of free hydroxide groups. The band in the range of (2945-2845) sm$^{-1}$ characterizes the valence vibrations of CH- and CH$_2$- groups. The absorption which occurs at the wave length of 1740 sm$^{-1}$ designates tightly associated water that belongs to carbohydrate and lignin components. The bands of absorption in the region of (1507, 1451, 1421) sm$^{-1}$ point at the presence of aromatic compounds in the content of wood, and they belong to the skeletal vibrations of aromatic ring. Very wide and intensive band at (1190-900) sm$^{-1}$ refers to the vibrations of simple aliphatic ethers and to carbohydrate skeletons [6, 7].

![Figure 3. IR-spectrum of wood-cement composition modified by oxalic aldehyde after 28 days of samples hardening.](image)

The main differences of IR-spectra of wood-cement composition (Figure 3) from IR-spectra of wood (Figure 2) are the following. The shift of valence vibrations peak for O–H bond in the region of a longer wave’s length is observed. The bands of absorption in the region of aromatic compounds vibrations are practically absent. The narrow and intensive bands in the region of 1396 and 872 sm$^{-1}$ are revealed. The region of cellulose spectra (1500–900) sm$^{-1}$ characterizes different vibrations of C–H, C–O and O–H - bonds, the vibrations of glycoside bond and glucopyranose ring of cellulose, skeletal vibrations of guaiacil ring C$_{Ar}$–O–C. Except that the intensity of bands in this region is sensitive to the nature of substituting components in the structure of chemical compounds [8-11].

The essential changes in IR-spectra of the samples speak for the complicated chemical and structural interactions in the system of WCW modified with oxalicaldehyde. Taking in to consideration the fact that processes of chemical interaction occur in the region of alkaline condition (pH=12), these changes are connected with lignin, cellulose and other wood components destruction. Microphotographs (Figure 4) of the initial sawdust and of that modified with oxalic aldehyde, and also of wood-cement composition being compared with the compressive strength of the samples show that the largest strength of WCW samples is achieved in the case when the surface of wood is partially covered with oxalic aldehyde or with the product of its interaction (Figure 4b). These conditions are reached at the concentration of oxalic aldehyde that equals to up to 2 mass. % from the mass of water.
It should be noticed that the optimal concentration of oxalic aldehyde for a cement stone equals to only 0.16 mass. % (Table 1), that indirectly confirms the processes of ethandial with chemical components of sawdust interaction. During the injection of 3 and more mass. % of oxalic aldehyde the strength of modified samples becomes comparable with that of control samples (Figure 1b). Taking into consideration the fact that cement grout fully covers the surface of wood aggregate (Figure 4c) the contact of cement with the surface of pure wood is considered to be an important moment for strength of WCW structures improvement.

On the basis of obtained experimental results the following reasons for the increase of WCW strength modified with oxalicaldehyde can be suggested.

1. It is known that bakelite is formed at the room temperature and condensation of phenol with formaldehyde in the presence of alkaline condensing substances [12]. Bakelite is a solid substance possessing strength. Since oxalicaldehyde is the analogue of formaldehyde, and the wood comprises phenols and aromatic rings in the structures of lignin and cellulose, and also the alkalinity of the medium (pH = 12) is created as a result of cement hydrolysis, one of possible chemical transformations can occur according to the scheme presented in Figure 5. The data of IR-spectra confirm this fact indirectly.

![Figure 5. The simulated scheme of lignin structure transmission into bakelite structure.](image)

2. Oxalic aldehyde suppresses water and gradually returns it in the system of structural new compounds in the later setting time that can increase the degree of cement particles hydration. Even after 28-day hardening the characteristic frequencies which correspond to the water with a normal web of hydrogen bonds and to that with the destructed structure are presented on the obtained spectrograms (Figure 3).
4. Conclusion
The effectiveness of oxalic aldehyde aquatic solution application in the systems based on cement was shown in the paper. The injection of a chemical additional agent having optimal concentration was determined to regulate the time of cement stone setting, to increase the compressive strength of the samples. The effect of compressive strength of the samples improvement is clearly revealed for the system of wood-cement composition modified with oxalic aldehyde. The optimal concentrations of a chemical additional agent to the system based on cement were detected.

Some possible interactions of ethandial with components of wood were studied by means of IR spectroscopy. It was shown that in alkaline conditions created by the products of cement minerals hydrolysis the destruction of wood components are fulfilled. Some possible mechanisms of the strength improvement for the modified wood-cement compositions were proposed.

References
[1] Gorlenko N P, Sarkisov Yu S and Volkov V A Bulletin of Higher Institutions “Physics” 127
[2] Lotov V A 2008 Problems of Geology and Expansion of Resources: col. of scientific papers of XIII International Symposium (Tomsk: Tomsk politechnical university) p 819
[3] Pichugin A P, Denisov A S and Khritankov V F 2005 Building Materials 5 2
[4] Nelson M L and O’Connor R T 1964 Journal of Applied Polymer Science 8 1311
[5] Nizina T A 2012 Influence of Mineral Additives on Rheological and Strength Characteristics of Cement Composites Vestnik of TSUAB 2 148
[6] Belamy L 1963 Infrared spectroscopy of complicated molecule (Moscow: Publishing house of foreign literature)
[7] Дехант И, Данц Р, Киммер В и Шмонсе Р 1976 Инфракрасная спектроскопия полимеров (М.: Химия)
[8] Hergert G L 1960 Infrared Spectra of Lignin and Related Compounds. II. Conifer Lignin and Model Compounds Journal of Organic Chemistry 25 405
[9] Zhabanov R G 1964 Infrared spectra of cellulose and its derivatives (Minsk: Nauka i Tekhnika) edited by Golman L P and Reznikov V M 1973 Journal of Applied Spectroscopy 19 494
[10] Pilipchuk Yu S, Pen R Z and Phinkelshtein A V 1965 Journal of Physical Chemistry 39 1768
[11] Chemical Encyclopedia 1988 edited by I L Knuyantsa (Moscow: Publishing house Soviet Encyclopedia) 1