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Control of Structurization Processes in Wood-Cement Systems at Fixed pH

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Abstract. The paper presents a study of structurization processes in the wood-cement systemmixed with the buffer solutions and the improvement of service properties of products produced therefrom. Infrared spectroscopy, X-ray phase analysis, and pH measurements show that structurization processes in wood-cement systems depend on the acidity of aqueous solution, the behavior of hydration, neutralization, and polycondensation reactions with the formation of polymer products including those with cement grout components and functional groups of wood. It is shown that phosphate buffer solutions used for mixing wood-cement compositions improve their strength properties and reduce water absorption. The optimum acidity of the buffered medium for service properties of the wood-cement systemis pH = 4.8.

INTRODUCTION

Wood-fiber cement composites are widely used in modern construction industry. The products based on wood-fiber composites are characterized by low cost, low production technology, and environmental safety. The raw material is usually large tonnage forest products with the annual output of about 32000 m^3 the utilization of which assists to the environmental protection. At the same time, the development of efficient materials with the enhanced service properties becomes relevant due to the increased requirements for the quality of products. This is because the wood fiber is a hydrophilic raw material and used as inert filler.This property exerts a negative effect in using construction products [1-4]. Thus, investigations of structurization processes in the wood-cement system accounting for the wood chemical composition, its behavior in introducing chemical additives of low concentrations, low-energy activation by external effects will allow not only improving the service properties of end products but also producing construction materials with predictable properties.

As is known, the acidity control of mixing solutions results in modification of physicochemical parameters of the hardening cement-based composition and, as consequence, modification of processing properties of the cement-water system [5,6]. A mechanism of these phenomena is not quite clear. It is supposed that pH decrease in water evokes the reaction of neutralization that decreases hydration rate, setting timethat results in the strength decrease of the whole cement brick. The structure formation is considerably complicated when such chemical active component as wood is introduced in the composition. It should be noted that investigation results obtained in this field are still being debatable.

MATERIALS AND METHODS

The phosphate buffer solution was prepared in the following way. 96.9 ml of disodium phosphatesolution with 0.07M concentration was placed in 100 ml measuring flask and diluted with potassium phosphate monobasic solutionwith 0.07M concentration up to the mark. Phosphate buffer solutions were obtained at different concentrations at pH of 4.8, 7.0 and 8.5 which were used in the capacity of a mixing solution.

The wood-cement composition consisted of the type M500 Portland cement and wood aggregate in the form of softwood sawdust. Preliminary wet sawdust was mixed with Portland cement and placed in $(5\times5\times5)\times10^{-2}$ m

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moulds. The specimens have been cured in amoisture chamber for 28 days at (20±2) °C and (70±10) % relative humidity. Then each specimen was unmolded in a day and stored in amoisture chamber until the experiment.

The infrared spectrophotometer SPEKORD was used for the material identification within the wave range of 4000 – 400 cm^{-1}. The specimens were prepared by the KBr disk technique.

XRD analysis was carried out by DRON-3diffractometerusing the ionizing recording method. An X-ray tube with iron anode was used. Specifications for the DRON-3 included $25\cdot10^{-3}$ V voltage; 8A current intensity; 2 °/min goniometer rotation rate at (293+2°) K. The intensity of diffraction maximums was measured on a 10-point grading scale of relative units.

To detect water absorption, the specimens were placed in a flask with water with 5 cm of water above them. After 48 h, water-filled specimens were then weighted on scales with the balance accuracy of 0.02 g, and water absorption was measured by the mass difference.

EXPERIMENTAL RESULTS AND DISCUSSION

The experimental findings show that the compressive strength in specimens mixed with the neutral phosphate buffer solution (pH=7) does not practically change as compared to the test specimen, while in specimens mixed with alkaline and acidic solutions, it significantly increases. At the same time, the highest strength and the lowest water absorption within the 28 day period of hardening are achieved for the phosphate buffer solution at pH = 4.8 (see Fig. 1 and the Table 1 below).

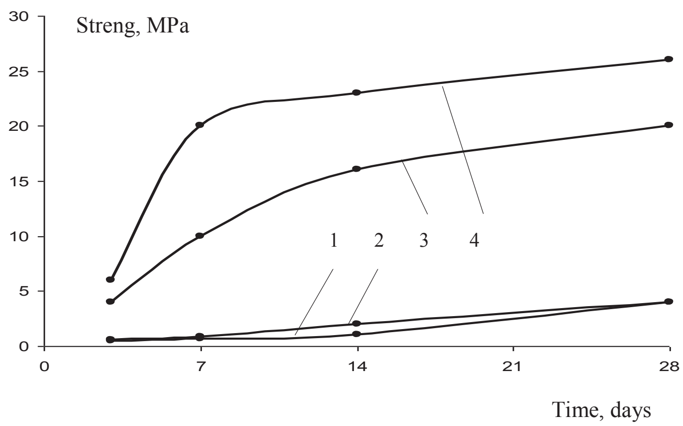


FIGURE 1. Kinetics of strength generation of wood-cement composition: *1*– withH_2O; *2*– with phosphate buffer solution (pH=7.0); *3*– with phosphate buffer solution (pH=8.5); *4*– with phosphate buffer solutionpH = 4.8

TABLE 1. Water absorption of wood-cement specimens depending on pH of phosphate buffer solution

Wood-cement system	Water absorption, %
phosphate buffer solutionpH=4.8	5.0
phosphate buffer solutionpH=7.0	8.5
phosphate buffer solutionpH=8.5	10.0
H_2O	11.0

As shown in Fig. 2, the transmission curves do not practically change in mixing the wood-cement system with phosphate buffer solutions regardless pH medium. Therefore, the new formations in compositions under study are of the similar nature.

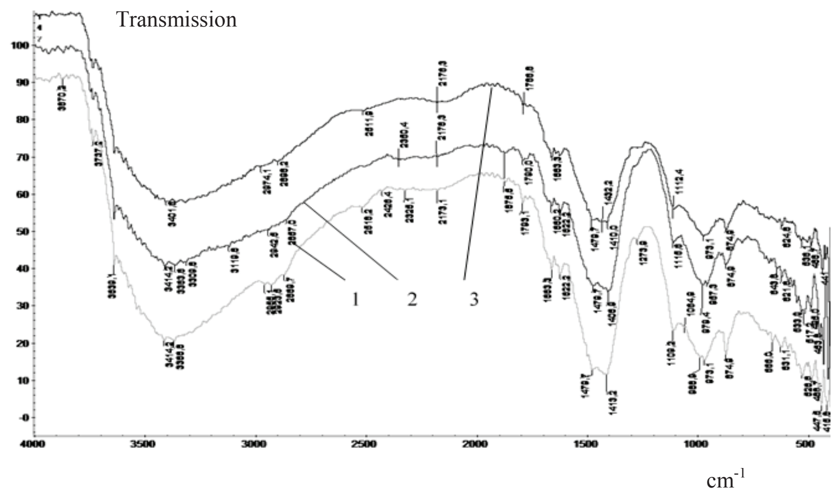


FIGURE 2. IR transmission spectrums of wood-cement systems mixed withphosphate buffer solutions at different pH values: *1*–4.8; *2*– 7.0; *3*– 8.5

The main differences are observed in the regions of (1500-1700) cm^{-1} and (2800-3000) cm^{-1}. Also, the IR spectrum includes four groups of absorption bands in the regions of (670–790), (860–1030), (1085–1160) and (1255–1290) cm^{-1}, that makes possible to refer anion of obtained composition to the polyphosphate type. The effect of polymerization degree and the type of cation are reflected in the shift of the absorption band maximums of O-P-O and P-O-P groups to the long-wave region and also in the change of the absorption band intensity both within the detected groups and between them [7,8].

The results of the XRD analysis of specimens mixed with distilled water (pH=7) and phosphate buffer solutionsshowthe mineral identification presented in Figs. 3 and 4 [9,10].

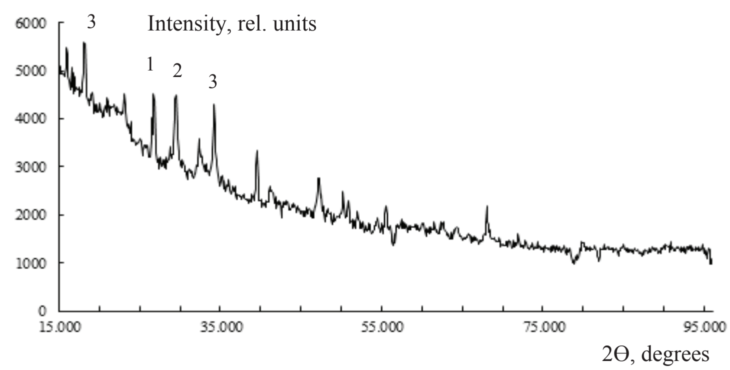


FIGURE 3. XRD patterns of wood-cement system mixed with water

The analysis of XRD patterns shows that the intensive lines of alite mineral (C_3S) are presentedin test specimen that indicates to the hydration process retardation in presence of the extractive water-soluble substances of wood (Fig. 3). On the contrary, C_3S is almost completely hydrated that is reflected by the change in intensity of its diffraction maximums (Fig. 4). Moreover, diffraction reflections typical for dicalciumand monocalcium phosphate are observed. As is known, in acidic mediahardly solubledicalcium phosphate(0.02solubility product) is mainly formed, while in alkaline media, highly solublemonocalcium phosphate is observed. In the authors' opinion, this fact is one of the reasons of the higher strength of specimens as compared to the use of alkaline mixing solution (Fig. 2).

The observed effects are conditioned by the variety of structurization processes occurred in the wood-cement system that are underlain by hydration reactions of acid-base interaction, neutralization and condensation polymerization with the formation of polymer products of the linear and branched types, and chemical reactions with hydration products of cement and functional groups of wood. The main contribution to the development of the structure formation of the wood-cement system is made, first, by the property of the phosphate buffer solution to maintain the consistency of acidity in the medium within the narrow pH range (Fig. 4) that facilitates the formation of new structures with similar chemical compositions.

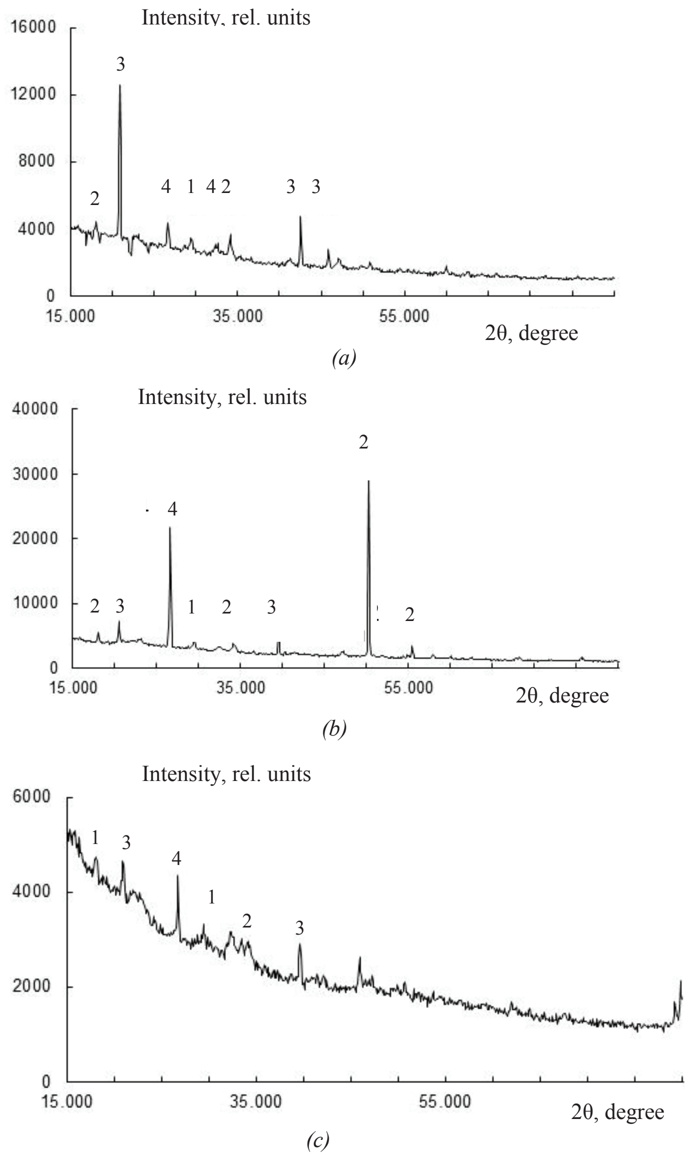
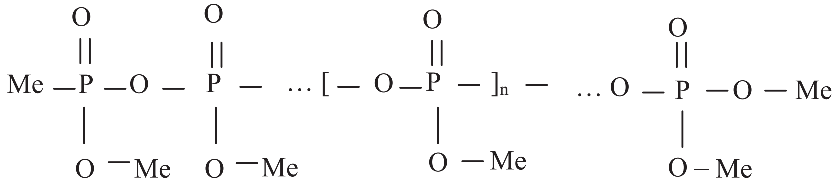


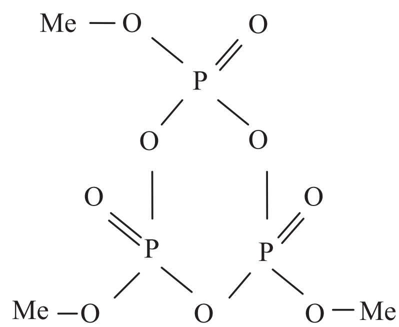
FIGURE 4. XRD patterns of wood-cement system mixed with phosphate buffer solutions at different pH values: *a*–4.8; *b*–8.5; *c* – 7; *1* - alite (C_3S); *2* - hydrous calcium silicate; *3*–Portland cement $Ca(OH)_2$; *4*–calcium phosphate dehydrate $Ca_3(PO_4)_2{\cdot}2H_2O$

And second, the processes of polymerization that involve phosphate ions resulting in strengthening the wood-cement system (Fig. 2) due to the formation of linear and cross-linked bulk structures. As described in the work of Kuznetsova *et al.* [11], polymer phosphates of different structural types can be presented by the following chemical structures.

1. Linear polyphosphates: $Me_{n+2}P_nO_{3n+1}$,



2. Ringmeta phosphates $Me_nP_nO_{3n}$, or



where is the degree of polymerization (2<n>50).

3. Branched phosphates (ultraphosphates) that are combinations of rings and chains with the common chemical formula of anion.

As described in the literature [11], these structures can be formed during the process of neutralization of phosphate compounds. The condition of the neutralization reaction process is created due to the alkaline medium of the cement aqueous solution. If calcium in this case is presented by Me, then such structures are considered to be hydrophobic that provides the decrease of water absorption by the specimens. The chemical interaction between the products of cement mineral hydration is supported by Fig. 3 and Table 1. In adding water in a dry mixture of cement and wood, the hydration reaction of tricalium silicate is observed in the first turn [12]:

$$3CaO\times SiO_2\times(n+1)\times H_2O= 2CaO\times SiO_2\times nH_2O+ Ca(OH)_2. \qquad (1)$$

Then the exchange reactions occur:

$$Ca(OH)_2+ NaH_2PO_4 = Ca(H_2PO_4)_2+ H_2O;$$
$$Ca(OH)_2+ Na_2HPO_4 = CaHPO_4 + H_2O.$$

If the system contains a phosphate buffer solution, OH^- group bonding takes place.According to the Chatelier's principle, changes occur that shift the equilibrium to the formation of dicalcium silicate (1) that is proved by the XRD analysis. As consequence, the processes of hydration of the cement mineralogical component are accelerated and crystal phases of new formations with typical sizes are formed,thereby increasing the material strength at early stages of the structure formation (Fig. 1).

The role of wood is reduced to the involvement in hydrolysis and exchange reactions between functional groups. In alkaline medium, the degradation of cellulose is mostly observed long with keto/enoltautomerization and isomerization reactions and carbon chainaminolysis.

CONCLUSIONS

1. It was shown that phosphate buffer solutions used for mixing wood-cement compositions improved their strength properties and reduced water absorption.
2. The higher service properties of the wood-cement system are provided by pH = 4.8 that was considered to beoptimumfor the buffered medium.
3. Some of mechanisms of observed effects were the acceleration of such processes as alite hydration, chemical interaction between hydration products of cement minerals, polymerization involving phosphorous compounds, and wood hydrolysis.

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