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The Influence of Organic and Mineral Additives on Hydration of Cement

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This paper describes the inhibitory impact of water soluble extractives in wood sawdust on Portland cement setting. It was determined that pozzolanic mineral additives (e.g. opoca) eliminate this harmful influence of extractives. Fresh sawdust extracts of Lithuanian wood's species (the fir, the alder, the asp, the hornbeam and the birch) have been analyzed in the article. Alkali medium dissolves much more wood's extractives, than water. The influence of extractives' additive on binding material (pure cement and cement with opoca additive) was estimated according to the setting time of binding material paste, chemically combined water changes, cement stone strength and X-ray diffraction of hardened cement stone.

The efficiency of mineral additives depends on its pozzolanic activity. The influence of specific surface (grinding degree) of opoca on CaO binding rate and pozzolanic activity was determined, and relation between adsorption power of opoca and its specific surface was investigated.

Keywords: wood extract, cement paste, opoca, pozzolanic activity, setting time, specific surface area, adsorption.

INTRODUCTION

Building products made from wood aggregates and mineral binding materials are widely applied in many developed countries. In this case specially prepared wood aggregates are employed, but wood sawdust practically is not used.

It has been found, that soluble sugars and a part of hemicellulose, which under certain conditions can be resolved to these sugars have a negative effect on cement's hydration [1, 2]. Sugars in concentration as low as 0.03…0.15 wt. % in cement will retard the setting time and the strength of the cement [3].

The main sugars of different wood's species extracts are glucose and gallactose (75…90 %), arabinose (10…15 %) and xylose with manose (1…3 %). They are the main components of all extracts. Composition of alkali extracts is similar to composition of water extracts [4]. Extraction temperature has not an essential influence on the extract's qualitative composition. Other soluble materials have not an important influence on the hydration of cement.

The alkali medium of cement paste stimulates extracts' exudation [3, 4]. When pozzolanic material is added to the cement, free $Ca(OH)_2$ and active silica can combine and form silicate hydrates, which are not soluble in water. This reduces amount of free $Ca(OH)_2$ and, herewith, pH of system [6].

Concentration of soluble wood materials in extract depends on extraction time and temperature [5]. The longer extraction time and the higher temperature (till 100 ºC) afford to higher concentration of soluble materials.

After the summarizing of the results of investigation [2, 7, 8] the hypothesis that wood sugars are surface activating hydrophilic materials, was formed. Inserted to the cement mixtures together with hardening water under the influence of adsorption power and cohesion of molecules, sugars form thin adsorption layer on the surface of cement grains. The small cement parts covered with this film cannot aggregate. Thus, water cannot reach the grains of cement, and the migration of hydration products is impossible. It slows down the hydration of cement.

Mineral additives added to the mixture improve the quality of concrete, which has organic additives [9, 10]. Their influence isn't sufficiently investigated and their application is low.

The aim of the present work is to study the influence of the wood extractives on the setting properties of cement and the influence of the opoca on the process.

MATERIALS AND METHODS

The materials used in this investigation were Portland Cement CEM I 42.5R, Portland Cement CEM I 32.5 and ground carbonate opoca. The chemical oxide composition of starting materials used is shown in Table 1.

Extracts of wood were prepared from fresh sawdust of various woods' species (the fir, the alder, the asp, the hornbeam and the birch). The sawdust was poured with water (water extracts) or with cement suspension (alkali extracts). The flasks with mixture were tightly closed and kept 24 hours at the temperature of 80 ºC. Sometimes the mixtures were mixed up. Later extracts were separated by vacuum filtration and evaporated in water bath. The residues have been dried at the temperature of 80 ± 5 ºC. The amount of $Ca(OH)_2$ formed in alkali extracts was subtracted.

The cement pastes and cement-opoca pastes were prepared using the standard water and wood extracts. The fresh pastes were moulded in 2×2×2 cm steel moulds. One part of pastes were first cured in the laboratory within their moulds at 20 ºC with 90 % relative humidity for 24 h. Other part of pastes were steamed within the moulds at 100 % relative humidity and temperature 80 ºC for 8 h.

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Table 1. The data of chemical composition of raw materials

Raw materials	Composition, %							
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	R_2O	SO_3	Ignition loss
Cement	21.33	5.28	2,95	65.37	2,08	1.51	1.12	0.81
Carbonate opoca	55.83	2.31	1.07	21.06	0.49	0.52	0.58	18.18

Table 2. The data of extracts of various wood's species, when extraction was carried out 24 hours at temperature of 80 °C

Wood's species	Amount of extracted materials, % from wood	
	10 g of sawdust and 10 ml of water	10 g of sawdust, 2.5 g of cement and 10 ml of water
The fir	1.202	5.087
The alder	0.904	6.576
The asp	1.326	7.433
The hornbeam	1.215	8.407
The birch	1.313	10.586

Then the specimens were demoulded, placed under water and cured for 28 days at 20 ºC.

After the predetermined curing time, the hydration of cement was stopped by grinding in acetone–methanol mixture and samples were dried at the temperature of 100 ºC. The changes in the mechanical and physical properties of the specimens were examined for compressive strength, amount of chemically combined water, and X-ray diffraction analysis (XRD).

The X-ray phase analysis has been conducted using DRON-3 diffractometer. The investigation has been carried out in the θ range 3 – 30° with Ni – filtered the Cu K_α radiation.

The specific surface area of different fractions of opoca has been determined by Blain's method.

Opoca activity was determined according to its capacity to bind $Ca(OH)_2$ from the lime solution. It is expressed in the quantity of CaO mg for 1 g of the material.

Concentration of glucose was determined by method of iodometric adsorption.

RESULTS AND DISCUSSIONS

At the first stage of experiment the fresh sawdust extracts of Lithuanian wood's species (the fir, the alder, the asp, the hornbeam and the birch) were investigated. The sawdust was treated under two different conditions: (1) neutral (water), (2) base (cement suspension). Test results are given in Table 2. It was estimated, that in alkali solution it dissolves 5…10 times as much wood's extractive materials, than in water.

The results of investigation correspond to the references data and corroborate the great influence of hemicellulose, which present in wood on the concentration of extracts. Under the influence of $Ca(OH)_2$ hemicellulose disintegrates to the soluble sugars.

The findings confirm that there is the least amount of soluble materials in fir. Deciduous trees have much more soluble materials.

It has been confirmed that water soluble wood's sugar slows down hardening and hydration of cement, the pozzolanic mineral additives (e.g. opoca) decrease this harmful influence. The mechanism for retardation of cement hydration by sugars is only partly understood. Therefore, the influence of extractives' additive on binding material (pure cement and cement with opoca additive) was estimated according to the setting time of binding material paste, chemically combined water changes, cement stone strength and X-ray diffraction of hardened cement stone.

In order to study the effects of wood's extracts on the setting time of binding material water extracts of various wood's species (the fir, the alder, the asp, the hornbeam and the birch) were prepared, then mixed with cement CEM I 42.5R and binding material, which was prepared from equal shares of this cement and grind opoca (Table 3).

Different amount of water-soluble materials in various species of wood has different influence on the *setting time of cement paste* (Table 3). Increasing the amount of additive increases the extent of retardation. X-ray phase analysis of these materials revealed hydration of cement and binding material, which harden in natural conditions. The small concentration of water-soluble materials of various woods' species results the same hydration as control samples'. When the concentrations are low, the amounts of formed new formations in various mixtures are the similar, thus it is impossible to observe them in X-ray phase analysis.

Because the X-ray phase analysis of samples, prepared applying extracts of various wood's species is the similar and there is only a small difference in intensity of some peaks, it is possible to maintain that hydration depends on the extract's concentration and doesn't depend on wood's species.

For the revelation of influence of soluble wood's materials on the hardening of cement the more coarse-grained cement CEM I 32.5, which hardening rate is lower and binding material, prepared from equal shares of this cement and grinded opoca were applied. They were mixed with wood's alkali extracts, which concentrations respectively were 1.604 % and 1.943 %.

Table 3. Influence of wood's extractives additives on the setting time of cement CEM I 42.5R and binding material (50 % of cement CEM I 42.5R + 50 % of opoca) pastes

Extract	Concentration of extract, %	Amount of additive by weight of cement, %	Setting time, hour-minute		Amount of additive by weight of binding material, %	Setting time, hour-minute	
			Initial set	Final set		Initial set	Final set
The water	–	–	5 – 50	7 – 35	–	2 – 20	3 – 15
The birch	0.155	0.047	5 – 50	6 – 45	0.059	2 – 10	2 – 50
The alder	0.255	0.077	6 – 30	10 – 20	0.097	2 – 50	3 – 20
The fir	0.338	0.1025	8 – 05	9 – 25	0.129	2 – 20	3 – 40
The hornbeam	0.341	0.103	7 – 35	9 – 30	0.130	2 – 35	3 – 55
The asp	0.392	0.119	8 – 05	11 – 10	0.149	2 – 30	3 – 40
Concentrate	0.738	0.223	9 – 20	12 – 40	0.281	3 – 05	4 – 15

Table 4. Influence of wood's extractives additives on the setting time, compressive strength and chemically combined water of steamed and later 28 days cured cement CEM I 32.5 and binding material (50 % of cement CEM I 32.5 + 50 % of opoca) pastes

Extract	Concentration of extract, %	Amount of additive by weight of binding material, %	Setting time, hour-minute		Compressive strength, MPa / Amount of chemically combined water, %	
			Initial set	Final set	After steaming	After 28 days
Binding material – cement CEM I 32.5. The water/cement ratio of all samples – 0.235						
Water	–	–	3 – 45	4 – 45	60.08/10.15	78.58/11.68
Extract 1	1.604	0.377	5 – 30	6 – 20	49.75/9.92	52.92/11.27
Extract 2	1.943	0.457	13 – 20	16 – 40	17.42/6.69	43.17/9.78
Binding material – 50 % of cement CEM I 32.5 + 50 % of opoca. The water/cement ratio of all samples – 0.37						
Water	–	–	1 – 55	2 – 35	30.88/6.67	34.60/10.21
Extract 1	1.604	0.593	2 – 35	3 – 05	29.46/6.61	33.67/9.95
Extract 2	1.943	0.719	3 – 10	3 – 50	31.34/6.76	35.10/10.50

Samples were steamed at the temperature of 80 °C. Before steaming they were kept in the isothermal conditions for 4 hours. Samples were treated immediately after steaming and 28 days of hardening in natural conditions. The data were compared with the data of control samples, which were mixed with water. Results of investigation are presented in Table 4.

It was determined that influence of soluble wood's materials is the same on both kinds of cement – CEM I 42.5R and CEM I 32.5, when they harden as pure binding material and with opoca additive.

Amount of chemically combined water (water that participates in the reaction) determines the degree of cement's hydration. It was determined that extracts' additives in both classes of cement (without opoca) decrease the amount of chemically combined water in cement stone with respect to control samples. When cement was hardened in natural conditions the decrease of amount of chemically combined water was not big. Only at initial period of hardening (till 3 days) it was some more distinct. The steaming of reduced activity cement CEM I 32.5 with the addition of more concentrated wood's extract afforded bigger decrease of amount of chemically combined water in cement stone in comparison with control stone. After 28 days of hardening in natural conditions this difference decreases.

When binding material of cement with opoca additive was steamed there was the similar amount of chemically combined water in the composition of cement stone with soluble wood's materials in all cases with respect to control samples (Table 4).

When binding material of cement without additive of opoca was steamed, water-soluble wood's materials retarded the hydration of cement. The increasing concentration of these materials considerably decreases the *compressive strength* of steamed cement stone. Wood's extractives additives (0.457 % by weight of cement) decrease compressive strength after steaming 3.45 times with respect to control samples. After subsequent 28 days hardening in natural conditions of samples this difference has decreased, but still they got 1.82 times weaker than control.

When even high concentration extracts was added to the paste of binding material formed from 50 % of cement CEM I 32.5 and 50 % of opoca, the compressive strength of steamed samples becomes the same or bigger than the strength of control samples. In this case the additive of opoca absolutely abolishes harmful influence of water-soluble wood's materials on the hydration of cement.

The negative influence of water-soluble wood's materials on hydration of cement is explained by adsorption. Sugar inserted to the cement systems with hardening water orientate around the cement's grain and

form the adsorption layer decreases. By the way, more water is required for th. Therefore, the cement grains under the action of molecular forces lose the possibility to cohere and coagulate. The water cannot reach the grains of cement because of this layer.

The additive of pozzolanic mineral materials (e.g. opoca) to the cement mixtures decreases the influence of wood's extractives. Because the specific surface of pozzolanic additives is much more bigger than the cement's and the sorption power of these materials is increased, the adsorption of water soluble wood's materials first of all take place on the surface of pozzolanic materials and the concentration of extracts e preparation of mixtures of cement and pozzolanic additives. Therefore, water easily gets to the grains of cement and the hydration conditions become more favourable.

On the *X-ray diffraction patterns* of steamed samples of cement's stone, which was made with more concentrated extracts (0.457 % by weight of cement), the distinct peaks of minerals of hydrated clinker were seen and it shows low degree of cement hydration (Fig. 1).

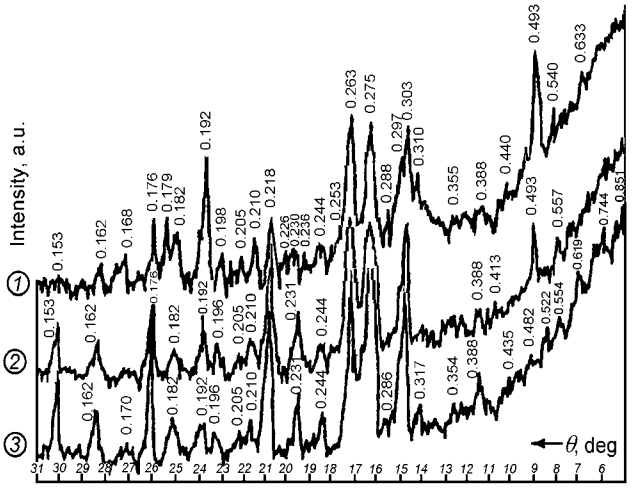

Fig. 1. X-ray diffraction patterns of cement CEM I 32.5: 1 – mixed with water and steamed; 2 – mixed with extract 2 and steamed; 3 – not hydrated cement

The X-ray diffraction patterns of samples of not hydrated cement (Fig. 1, curve 3) and the same steamed cement, which was prepared with wood's extract (Fig. 1, curve 2), was carried out. In this case intensive peaks, which interplanar distances d = 0.218, 0.176 nm (βC_2S and C_3S) and d = 0.231, 0.162, 0.153 nm (C_3S) showed, that there are a lot of not hydrated minerals in clinker in the cement stone. X-ray diffraction patterns of steamed cement, mixed with distilled water showed, that there are distinct peaks (d = 0.493, 0.310, 0.192, 0.179, 0.168 nm), characteristic to the main cement's hydration product $Ca(OH)_2$. The characteristic peaks of $CaCO_3$ (d = 0.387, 0.303, 0.249, 0.226, 0.210, 0.192, 0.162 nm) were identified too. Earlier mentioned peaks of hydrated clinker minerals were not intensive. It showed that hydration of cement without wood's extract additive is considerably more intensive.

X-ray diffraction patterns of samples of steamed binding material with opoca additive mixed with water (Fig. 2, curve 1) and samples with wood's extracts (Fig. 2, curve 2) were similar. The most characteristic peaks (d = 0.218, 0.178 nm) of not hydrated cement minerals were not intensive. It showed a large degree of cement's hydration. The distinct peaks of $CaCO_3$ (d = 0.387, 0.303, 0.249, 0.228, 0.209, 0.191, 0.188, 0.163, 0.160, 0.152 nm) and quartz peaks (d = 0.423, 0.333, 0.228, 0.197, 0.182, 0.154 nm) predominate in all X-ray phase analysis.

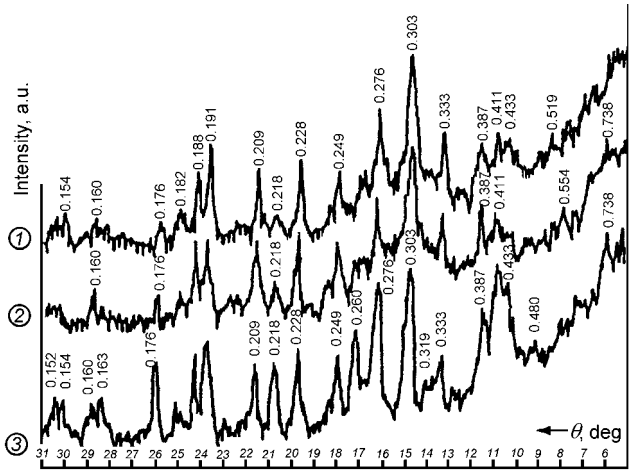

Fig. 2. X-ray diffraction patterns of binding material (50 % of cement CEM I 32.5 + 50 % of opoca): 1 – mixed with water and steamed; 2 – mixed with extract 2 and steamed; 3 – not hydrated binding material

$Ca(OH)_2$ was not identified for the steamed cement with opoca additive, because $Ca(OH)_2$ react with SiO_2, which present in opoca and CSH forms.

Our study confirmed the expediency of employment of mineral additives (opoca) with large specific surface. What is the influence of additive particle fineness on these processes isn't understood.

The aim of the third work's stage was to determine the influence of specific surface (the grinding degree) of opoca on CaO binding rate and pozzolanic activity, and to investigate the dependency of adsorption power upon the specific surface.

Five fractions (in mm) of opoca were employed for investigation: I – 0.9…0.63; II – 0.63…0.315; III – 0.315…0.14; IV – 0.14…0.05; V – < 0.05.

The data of determined conditional specific surface of different fractions of opoca are presented in Table 5.

Table 5. Specific surface area of different fractions of opoca

Fraction, mm	Specific surface area, m^2/kg
0.9…0.63	230
0.63…0.315	340
0.315…0.14	600
0.14…0.05	785
< 0.05	1125

It was determined that during the time the influence of opoca's specific surface area on binding rate of CaO was not constant (Table 6). At the initial stage of experiment (till 8 days) the largest opoca fraction (230 m^2/kg) bound

20…25 % of CaO less, than the smallest (1125 m^2/kg). Later this difference grew up and after 30 days it reached almost 50 %.

Table 6. The kinetics of binding of CaO with opoca of different specific surface area

Time, day	Specific surface area, m^2/kg				
	1125	785	600	340	230
	Amount of bound CaO, mg/g				
2	16	15	15	13	12
4	32	30	29	26	24
6	53	49	46	43	40
8	76	69	64	56	53
10	100	93	83	76	67
12	122	112	99	90	74
14	145	128	114	102	84
16	165	147	128	117	95
18	181	164	141	127	103
20	198	175	152	134	110
22	219	190	164	145	121
24	233	200	174	149	125
26	248	212	184	156	130
28	266	229	196	164	138
30	281	241	210	172	144

At the same time the pozzolanic activity (binding of CaO during the month (15 titration)) of opoca of different specific surface area was investigated (Fig. 3), because the references refer only data of samples gotten through the standard screen N 008. Pozzolanic activity depends greatly on the specific surface area of opoca.

It was determined, that equation $y = 15.2\,x^{0.41}$ describes the dependence of pozzolanic activity y of opoca upon its specific surface area x the most optimally.

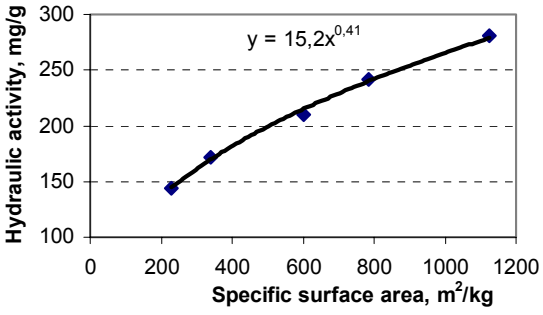

Fig. 3. The influence of opoca specific surface on its pozzolanic activity

Different fractions of opoca were poured with glucose (the main carbohydrate in extracts of different wood's species) solution concentration of 0.3 % and the dependence of its adsorption power upon the particle fineness was investigated. The mixture in some intervals of time was mixed up. After 2 and 24 hours remained concentration of glucose was determined by method of iodometric adsorption. The initial level of glucose solution's concentration was equated with 100 %. The data of glucose concentration level after 2 and 24 hours adsorption with an opoca of different specific surface area is given in Fig. 4.

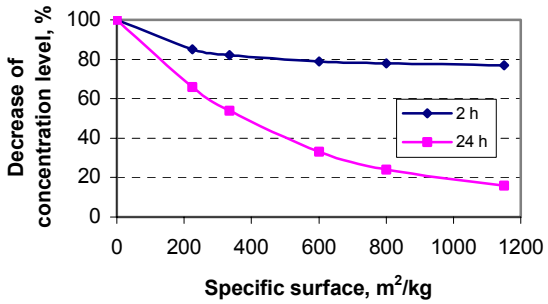

Fig. 4. The changing of 0.3 % glucose solution concentration after 2 and 24 hours adsorption with a opoca with different specific surface area

The data showed that at the initial stages of hardening of cement sawdust concrete the biggest influence of particle fineness of pozzolanic additive is on additive's adsorption properties. Immediately after mixing of sawdust concrete with water adsorption of separating wood extracts with an opoca began. Time to time a new proportion of extracts separated, but at the same time adsorption of it with an opoca grew up.

At later stages of hardening the influence of additive's particle fineness on binding of separating $Ca(OH)_2$ grew up. It can be maintained that the bigger fineness of pozzolanic additive was the reason of higher definitive compressive strength of concrete.

CONCLUSIONS

1. Alkali medium dissolves much more wood's extractives, than water. Under the influence of $Ca(OH)_2$ hemicellulose disintegrates to the soluble sugars.
2. Sugars retard the hydration of Portland cement.
3. Cement hydration, setting and hardening depend upon wood's extract concentration and don't depend on wood's species, and preparation method.
4. The negative influence of water-soluble wood's materials on hydration of cement can be explained by adsorption. Inserted to the cement systems with hardening water, sugar orients around the cement's grain and forms the adsorption layer. Therefore, the cement grains under the action of molecular forces lose the possibility to cohere and coagulate. The water cannot reach the grains of cement because of this layer.
5. The additive of pozzolanic mineral materials (e.g. opoca) to the cement mixtures decreases the influence of wood's extractives. Because the specific surface of pozzolanic additives is much more bigger than the cement's and the sorption power of these materials is increased, the adsorption of water soluble wood's materials first of all take place on the surface of pozzolanic materials and the concentration of extracts decreases.

6. The amount of free lime combined by pozzolanic material is an indication of its pozzolanic activity. This property depends greatly on the specific surface area of pozzolana. During the time the influence of opoca specific surface area on binding rate of CaO is variable.
7. The most optimally equation, which describes dependence of opoca pozzolanic activity (y) upon its specific surface area (x), is $y = 15.2\,x^{0.41}$.
8. At the initial stages of hardening of cement the biggest influence of particle fineness of opoca additive is on its adsorption properties.
9. At later stages of hardening the influence of opoca additive particle fineness on its pozzolanic properties (binding of separating $Ca(OH)_2$) grows up.

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