

CEMENT HYDRATION IN THE PRESENCE OF WOOD EXTRACTIVES AND POZZOLAN MINERAL ADDITIVES

GIEDRIUS VAICKELIONIS, RITA VAICKELIONIENE

*Faculty of Chemical Technology, Kaunas University of Technology
Radvilenu str. 19, 50254 Kaunas, Lithuania*

E-mail: gievaic@ktu.lt

Submitted February 4, 2005; accepted March 30, 2006

Keywords: Wood extract, Cement paste, Opoca, Pozzolanic activity, Specific surface area, Adsorption

In this work, the ability to reduce the harmful influence of wood extractives using the pozzolanic mineral additive, carbonated opoca, was investigated. The influence of various wood species extracts on the setting time and the hardening of two types of Portland cement, CEM I 42.5 R and CEM II/A-L 32.5, was searched. It has been found that cement hydration, setting and hardening depend upon wood extract concentration and do not depend on wood species and preparation method. The influence of extractive additives on binding material (pure cement and cement with opoca additive) was estimated according to the setting time of binding material paste, active portion of the reaction products of cement hydration changes, cement stone strength and X-ray diffraction of hardened cement stone. The investigation data show that wood extractives decrease the hydration of cement and pozzolanic additives effectively minimize this influence. The expediency of employing mineral additives (opoca) with a large specific surface was confirmed and that opoca surface was found to influence the binding rate of CaO. The opoca specific surface influences its pozzolanic activity and adsorption ability. At the initial stages of cement hardening the strongest influence of the particle fineness of opoca additive was observed on its adsorption properties. At later stages of hardening the influence of opoca additive particle fineness on its pozzolanic properties (binding of separating Ca(OH)₂) increased.

INTRODUCTION

Building products, such as cement-bonded particle-board (CBP), wood wool cement board (WWCB), cement bonded fibreboard, etc., made from mineral-binding materials and wood aggregates are widely applied in many developed countries. Chittenden [1] divides mineral-bonded wood composites into two distinct groups: (1) composites in which wood is incorporated as an aggregate in the mineral matrix (as fibres, sawdust, shavings or particles) and (2) composites in which the cement (or other mineral binder) acts purely as a binder, such as wood wool cement board or flake board. Mineral-bonded wood or other lignocellulosic composites are moulded or compressed blocks and panels containing approximately 30-70 % by weight of wood in various forms and 70-30 % of mineral binder [2]. Specially prepared wood aggregates with particular dimensions and varying in treatment are used for their production. Fibreboard is manufactured using wood strips 300-500 mm in length and 0.1-0.8 mm wide. Wood-Fibre Cement Blocks contain about 80 % of wood fibre, which has been specially treated to make them immune to rot or insect damage. The treatment also prevents sugars and tannins in the wood from reacting with the cement, which would interfere with proper

curing. The wood particles (thickness 0.3-5 mm, length 25-30 mm, width 1.6-4.8 mm) used in the manufacture of the block may be partially or fully comprised of post-industrial softwood, which is then mineralized with cement. In CBP, specially graded raw wood shavings and chips (length 3-30 mm) also are used; they are neutralized and mineralized, then bonded together with Portland cement.

Preparing concrete mixtures with fine sawdust requires big amounts of water. This water dissolves the extractive materials that retard the hardening of Portland cement. Besides, using sawdust, the input of cement increases in comparison with analogous materials in whose production specifically prepared wood filling material is used.

In comparison with specifically prepared wood aggregates, wood sawdust is practically not used.

Wood is chemically heterogeneous and its components can be divided into two groups: structural components of high molecular weight - natural polymer substances (cellulose, hemicelluloses and lignin), which are the major cell wall components; and non-structural components of low molecular weight (extractives and inorganic components). The content of polymer substances: cellulose 40-42 %, lignin 26-28 %, hemicelluloses 29-34 % and extractives 5-10 %.

Cellulose is insoluble in water, organic solvents and alkaline solution. It does not mediate under the influence of these materials.

Lignin is the most complex polymer among naturally occurring high molecular weight materials. It does not disintegrate under the influence of various organic solvents, alkaline solutions and water.

Hemicelluloses differ from cellulose by containing various sugar units with much shorter chains. It is a group of different polymers made up of 5 and 6 carbon sugars. They are soluble in alkali and some hardwood polyoses are even soluble in water. Disintegration of hemicelluloses to the constituents in the alkaline solution increases the amount of extractives. Hemicelluloses are more reactive than cellulose.

The extractives are non-polymeric (except pectins and condensed tannins) and may be separated from the insoluble cell wall materials by solving them in water or organic solvents.

The presence of extractives results in corrosion of metals in contact with wood, inhibition of setting of concrete, glue, and finishes, etc. [3].

Cement is an alkaline inorganic composite containing a surface hydroxyl group [4]. Wood, in general, inhibits the setting of cement with hardwood fibres, being the most inhibitory. It has been determined that heartwood is also highly inhibitory in the curing of cement [5]. Wood extractives were found to adversely affect the exothermic hydration characteristics of Portland cement, which in turn affects the wood cement compatibility [6].

The main inhibitor of cement hydration are wood fibre soluble sugars and part of hemicellulose, which under certain conditions can be resolved in these sugars [7, 8, 9]. It has also been found that along with sugars, starches and tannins can inhibit cement setting. Other extractives that cause problems in cement wood compatibility are resins and fatty acids, terpenes and terpenoids, simple sugars and salts [5]. Sugars in concentration as low as 0.03-0.15 wt. % in cement retard the setting time and affect the strength of the cement [10].

The main saccharides of different wood species are glucose and galactose, arabinose and xylose with mannose. The composition of alkali extracts is similar to that of water extracts [11]. The extraction temperature does not influence the extract qualitative composition. Other soluble materials have an insignificant influence on the hydration of cement.

The concentration of soluble wood materials in an extract depends on extraction time and temperature [10, 11]. A longer extraction time and a higher temperature (up to 100°C) afford a higher concentration of soluble materials.

The alkali medium of cement paste stimulates extract exudation [10, 11]. Pozzolanic material added to

the cement stimulates combination of free $\text{Ca}(\text{OH})_2$ and active silica giving water-insoluble silicate hydrates, thus the amount of free $\text{Ca}(\text{OH})_2$ and, herewith, the pH of the system decrease [12].

Set-retardation may be primarily due to retarding of the hydration of tricalcium silicate through the adsorption of organic admixtures onto calcium hydroxide. Adsorption onto the initial hydration products of tricalcium aluminate can also retard the further hydration [13]. The inhibition of cement hydration occurs when the calcium silicate hydrate nucleation sites on the originally positively charged surfaces are poisoned by sugar-acid anions [8, 14].

Our investigations [8, 15, 16] have resulted in the hypothesis that wood sugars are surface-activating hydrophilic material. Added to the cement mix together with hardening water, under the influence of adsorption ability and cohesion of molecules, sugars form a thin adsorption layer on the surface of cement grains. Small parts of cement cannot aggregate, and grains of cement become out of the reach of water. Thus, migration of hydration products becomes the impossible and hydration of cement slows down.

Mineral additives added to a mixture of concrete and wood fibre improve its quality [17, 18]. The influence of these materials isn't sufficiently investigated and their application is low.

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

EXPERIMENTAL

The materials used in this investigation were Portland Cement CEM I 42.5R, Portland Cement CEM II/A-L 32.5 and ground opoca. Pozzolana contains approximately 38 % of calcium carbonate, therefore it is called carbonated opoca. The calcite is evenly distributed in opal in the form of dispersal parties and rests of microorganisms. Quartz is in the form of very fine particles. The chemical and mineralogical composition and the specific surface area (Blaine) of the starting materials are shown in table 1.

Wood extracts were made from fresh sawdust of various wood species (fir, alder, asp, hornbeam and birch). The sawdust was poured over with water (water extracts) and with cement suspension (alkali extracts). For the estimation of the amount of soluble products of cement hydration, in parallel with the above-mentioned mixes in the same conditions cement suspension without sawdust was prepared. Tightly closed flasks with the mixture were kept for 24 hours at a temperature of 80°C and mixed up from time to time. Later the extracts were separated by vacuum filtration.

Table 1. Chemical and mineralogical composition and specific surface area (Blaine) of starting materials.

Specifications	CEM I 42.5 R	CEM II/A-L 32.5	Carbonate opoca
1. Chemical composition (wt.%)			
SiO ₂	20.37	18.63	55.83
Al ₂ O ₃	5.04	5.41	2.31
Fe ₂ O ₃	2.82	2.90	1.07
CaO	63.90	62.42	21.06
MgO	1.99	3.20	0.49
R ₂ O	1.44	0.89	0.52
SO ₃	2.73	2.86	0.58
LOI	1.71	3.68	18.18
2. Mineralogical composition (wt.%)			
C ₃ S	58.87	52.75	Opal ~ 46
C ₂ S	14.62	13.73	Calcite ~ 38
C ₃ A	8.60	9.41	Quartz ~ 7
C ₄ AF	8.56	8.68	Chalcedony ~ 3
Cc	-	6.00	Glauconite ~ 0.7
C \bar{S} H ₂	4.50	4.50	Muscovite ~ 0.6
3. Specific surface (m ² /kg)			
	420	350	1100

To evaluating the amount of extracted materials in extracts, they were evaporated in a water bath and the residues were dried at a temperature of $80 \pm 5^\circ\text{C}$. The amount of soluble products of cement hydration formed in alkali extracts was subtracted. The calculated difference between the obtained data on the sawdust cement water system and cement water system extraction showed the amount of wood extractive. 25 wt.% of cement were used to maintain the alkali medium in the system.

The cement pastes and cement-opoca pastes were prepared using the standard water and wood extracts. The monitoring of consistency and setting time were directly carried out using a Vicat apparatus.

The fresh pastes were moulded in 2 cm steel cubes. One part of them were kept in a 90 % relative humidity (R.H.) at 20°C for 24 h, and the others were steamed in a 100 % R.H. at 80°C for 8 h. Then all specimens were remoulded and kept under tap water up to 28 days at 20°C , then broken.

After the determination of the compressive strength, the hydration of pastes was stopped using a 1:1 mixture of methanol acetone and then the pastes were dried at a temperature of 100°C . Three samples of cement cubes were measured for each test, and the mean value was considered. The mechanism of hydration was also studied by the classical techniques, namely, chemically combined water measurements, XRD (X-ray diffraction) and DTA (differential thermal analysis).

The kinetics of hydration was followed by determining the active portion of reaction products of cement hydration by the ignition loss at 1000°C of the dried paste on an ignited weight basis minus the amount of ignition loss of the anhydrous binding material (in the first case pure cement and in the second case cement with opoca additive).

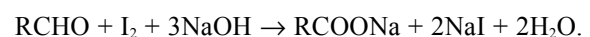
XRD analysis was performed using a DRON-3 diffractometer. The investigation was carried out in the 2θ range $10\text{-}60^\circ$ with Ni-filtered, Cu K α radiation.

The DTA analysis was performed using a Du Pont 990 thermal analyzer at a heating rate $10^\circ\text{C}/\text{min}$ up to 1000°C with finely powdered alumina as a reference material.

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

The opoca activity was determined according to its capacity to bind Ca(OH)₂ from lime solution. It was expressed as the amount of CaO mg in 1 g of the material.

The concentration of glucose was determined by the method of iodometric adsorption. This method is based on the ability of iodine in an alkali medium to oxidize the aldehydic group of the glucose molecule to the carboxylic group.



RESULTS AND DISCUSSION

At the first stage of the experiment, fresh sawdust extracts of various wood species were investigated. The sawdust was treated in two different conditions: (1) neutral (water), (2) base (cement suspension). The test results are given in table 2. It was estimated, that alkali solution dissolved 5-10 times as much of wood extractive material as did water. The results of the investigation correspond to the reference data [10,11] and corroborate the great influence of hemicellulose. Under the influence of Ca(OH)₂ hemicellulose disintegrates into soluble sugars. The findings confirmed that the lowest content of soluble materials in fir. Deciduous trees contained much more soluble materials.

Table 2. Data on extracts of various wood species when extraction was carried out for 24 hours at a temperature of 80°C.

Wood's species	Amount of extracted materials from wood (wt.%)	
	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

The investigation has confirmed that water-soluble wood sugars slow down the hardening and hydration of cement, and this harmful influence can be decreased using pozzolanic mineral additives (e.g., opoca). The mechanism of retardation of cement hydration with sugars has been only partly clarified.

The effects of wood extracts on the setting time of binding material were elucidated by investigating mixes of water extracts of wood species with cement CEM I 42.5R and binding material, which were prepared from equal parts of this cement and ground opoca (table 3). Different amounts of water-soluble materials in various species of wood had a different influence on the *setting time of cement paste* (table 3). Increasing the amount of the additive increased the extent of retardation. Using a

rapid-hardening cement, a low small concentration of water-soluble materials of various wood species resulted in the same hydration as in the control samples. Low concentrations resulted in similar amounts of new formations in various mixtures, thus, it was impossible to observe them in X-ray phase analysis.

To reveal the influence of soluble wood materials on the hardening of cement, more coarse-grained cement CEM II/A-L 32.5 with a lower hardening rate and a binding material made from equal portions of this cement and ground opoca were mixed with wood alkali extracts whose concentrations were respectively 1.604 % and 1.943 %. Then they were kept in the isothermal conditions for 4 h, steamed at a temperature of 80°C, hardened in natural conditions up to 28 days and immediately treated. The data were compared with the data on control samples prepared with water. The results are presented in table 4. The influence of soluble wood materials was the same on both kinds of cement, CEM I 42.5R and CEM II/A-L 32.5, when they harden as a pure binding material and with an opoca additive.

The active portion of the reaction products of cement hydration determines the degree of cement hydration. Extract additives in both classes of cement (without opoca) decrease the active portion of the reaction products of cement hydration in cement stone with respect to control samples. Hardening of cement in natural conditions only slightly decreased the active por-

Table 3. Influence of wood extractive additives on the setting time of cement CEM I 42.5R and binding material (50 wt.% of cement CEM I 42.5R + 50 wt.% 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 extractive additives on the setting time, compressive strength and active portion of reaction products of cement hydration of steamed and later for 28 days cured cement CEM II/A-L 32.5 and binding material (50 wt.% of cement CEM II/A-L 32.5 + 50 wt.% of opoca) pastes.

Extract	Concentration of extract (%)	Amount of additive by weight of binding material (%)	Setting time, hour-minute		Compressive strength, (MPa) /Amount of active portion of the reaction products (%)	
			Initial set	Final set	After steaming	After 28 days
Binding material - cement CEM II/A-L 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 wt.% of cement CEM II/A-L 32.5 + 50 wt.% 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

tion of reaction products. The general, in the initial period of hardening (up to 3 days) it was more distinct. Steaming of reduced activity cement CEM II/A-L 32.5 with the addition of more concentrated wood extract afforded a more significant decrease of the active portion of reaction products in cement stone in comparison with control stone. After 28 days of hardening in natural conditions this difference decreased.

When the binding material of cement with opoca additive was steamed, there was a similar amount of the active portion of reaction products of cement hydration in the composition of cement stone with soluble wood materials in all cases with respect to control samples (table 4).

When cement without opoca additive was steamed, water-soluble wood materials retarded the hydration of cement. Increasing the concentration of these materials considerably decreased the compressive strength of steamed cement stone. Wood extractive additives (0.457 wt.% of cement) decreased the compressive strength 3.45 times with respect to control samples. The subsequent 28-day hardening of samples in natural conditions reduced this difference to 1.82 times.

Even high concentrations of extracts added to the paste of binding material formed from 50 % of cement CEM II/A-L 32.5 and 50 % of opoca made the compressive strength of steamed samples the same or bigger than the strength of control samples. In this case, the addition of opoca absolutely abolished the harmful effects of water-soluble wood materials on cement hydration.

Referring to our study, we assumed that inserted to the cement systems with hardening water, sugar molecules keep around the cement grain and form an adsorption layer. Therefore, under the action of molecular forces cement grains lose the possibility to cohere and coagulate. The water cannot reach the grains of cement because of this layer. The formation of such layer is described in the references [8,13]. The negative influence of water-soluble wood materials on cement hydration is explained by adsorption.

The addition of pozzolanic mineral materials (e.g., opoca) to cement mixtures decreases the influence of wood extractives. Because the specific surface of these additives is much bigger than of cement and the sorption ability of these materials is higher, the adsorption of water-soluble wood materials first of all takes place on the surface of pozzolanic materials and the concentration of extracts decreases. By the way, more water is required for the preparation of mixtures of cement and pozzolanic additives. Therefore, water easily gets to cement grains and facilitates the hydration.

The distinct peaks of minerals of hydrated clinker on the X-ray diffraction patterns of steamed samples of cement stone, which was made with more concentrated extracts (0.457 wt.% of cement) showed a low degree of cement hydration (figure 1).

The X-ray diffraction patterns of non-hydrated cement samples (figure 1, curve 3) and the same steamed cement prepared with wood extract (figure 1, curve 2), were carried out. Intensive β - C_2S and C_3S peaks showed that there were many non-hydrated minerals in clinker in the cement stone.

On the X-ray diffraction patterns of steamed cement mixed with distilled water (figure 1, curve 1) distinct peaks characteristic of the main cement hydration product $Ca(OH)_2$ were seen. The characteristic peaks of $CaCO_3$ were identified too. The above-mentioned peaks of hydrated clinker minerals were not intensive, implying that cement hydration without wood extract additive was considerably more intensive.

X-ray diffraction patterns of samples of steamed binding material with opoca additive mixed with distilled water (figure 2, curve 1) and of samples with wood extracts (figure 2, curve 2) were similar. The most characteristic peaks of non-hydrated cement (figure 2, curve 3) minerals (β - C_2S and C_3S) were not intensive, showing a large degree of cement hydration. The distinct peaks of $CaCO_3$ and quartz predominated in all X-ray phase analysis.

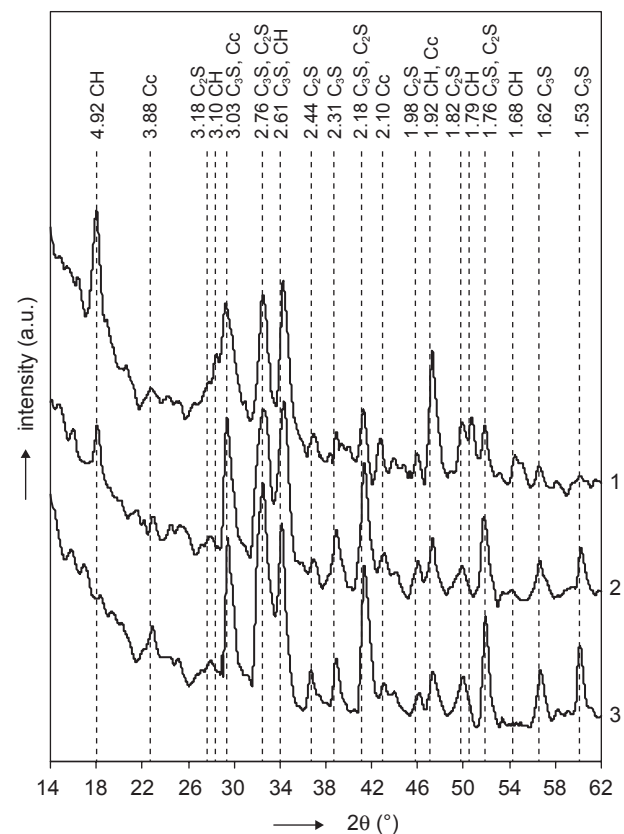


Figure 1. X-ray diffraction patterns of cement CEM II/A-L 32.5.; 1 - mixed with water and steamed; 2 - mixed with extract 2 and steamed; 3 - non-hydrated cement (C_3S - alite, β - C_2S - bellite, C_3A - tricalcium aluminate, CH - calcium hydroxide, Cc - calcium carbonate).

Ca(OH)₂ was not identified in the steamed cement with opoca additive, because Ca(OH)₂ reacts with opoca SiO₂ and forms CSH.

Figures 3 and 4 illustrate the DTA thermograms of the same samples. All DTA thermograms of CEM II/A-L 32.5 Portland cement (figure 3) show three main endothermic effects. The first and largest effect at a temperature of 150-200°C is the elimination of hygroscopic water and the dehydration of the obtained hydrosilicates. The second effect at a temperature of 470-490°C shows dehydration of Ca(OH)₂, and the third endothermic effect at a temperature of 725-740°C is essentially due to decarbonisation of CaCO₃.

The intensity of the endothermic effect at a temperature of 480°C of steamed Portland cement mixed with alkali wood extractive (0.457 % from Portland cement mass) (figure 3, curve 2) is lower than the intensity of Portland cement mixed with water (figure 3, curve 1). It shows that the addition of wood extractive slows down the hydration of cement. The low endothermic effect at a temperature of 465°C of not hydrated cement (figure 3, curve 3) can be coherent with the dehydration of α-C₂SH which through the hygroscopicity of Port-

land cement and the humidity of clinker additives (gypsum and limestone) was able to form during the partial hydration of clinker mineral C₃S.

The degree of Portland cement hydration depends on the concentration of wood extractive. The higher content of extractives decreases the hydration of cement.

The DTA thermograms of binding material prepared of equal amounts of Portland cement CEM II/A-L 32.5 and opoca (figure 4) show two endothermic effects at temperatures of 110-200°C and 785-800°C and one exothermic effect at 855-890°C. The first endothermic effect, exactly as in the case of Portland cement without opoca additive, shows elimination of hygroscopic water and dehydration of hydrosilicates; the second endothermic effect is essentially due to decarbonisation of CaCO₃ of opoca. The endothermic effect of dehydration of Ca(OH)₂ is not displayed, because Ca(OH)₂, which separates during the hydration when specimens are steaming, reacts with SiO₂ of opoca and forms CSH (I) type hydrosilicates. The exothermic effects at a temperature of 855-875°C confirm the formation of this type of hydrosilicates. This effect is principally related to the conversion of CSH (I) to volastonite. Unhydrated binding material has no CSH (I). The exothermic effect at a temperature of 890°C (figure 4, curve 3) is connected with the formation of volastonite from the CaO (decarbonisation of CaCO₃) and SiO₂ of opoca.

The DTA thermogram (figure 4, curve 2) of Portland cement with opoca additive and mixed with alkali wood extractive is almost identical to the thermogram (figure 4, curve 1) of binding material mixed with water and steamed. Thus, in both cases Portland cement hydration is almost the same.

The DTA analyses are in good agreement with XRD data. It shows that opoca is an effective additive which decreases the harmful influence of wood extractives on the hydration of Portland cement.

Our study confirmed the expediency of employment of mineral additives (opoca) with a large specific surface. The influence of additive particle fineness on these processes is not yet clear.

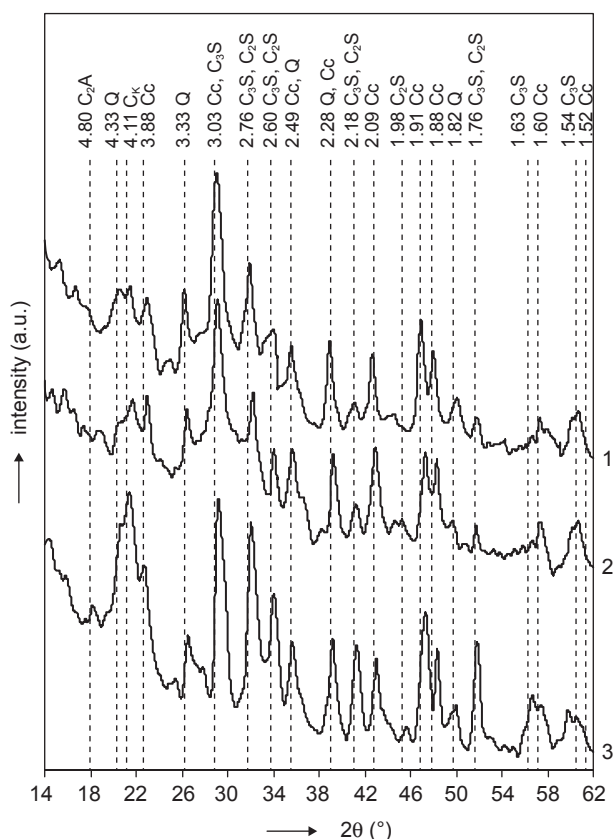


Figure 2. X-ray diffraction patterns of binding material (50 wt. % of cement CEM II/A-L 32.5 + 50 wt. % of opoca). 1 - mixed with water and steamed; 2 - mixed with extract 2 and steamed; 3 - non-hydrated binding material (C₃S - alite, β-C₂S - bellite, C₃A - tricalcium aluminate, Q - quartz, Cc - calcium carbonate, C_R - cristobalite).

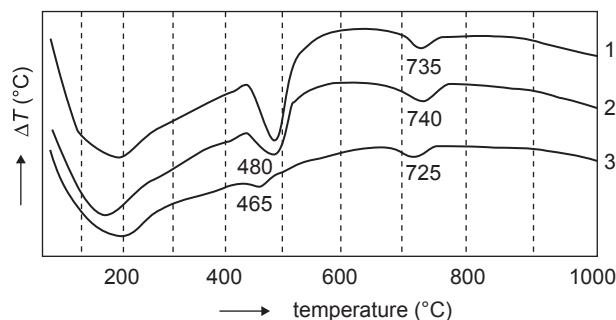


Figure 3. DTA thermograms of cement CEM II/A-L 32.5: 1 - mixed with water and steamed; 2 - mixed with extract 2 and steamed; 3 - non-hydrated cement.

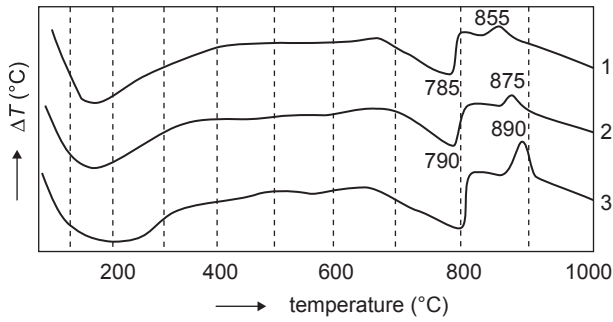


Figure 4. DTA thermograms of binding material (50 wt. % of cement CEM II/A-L 32.5 + 50 wt. % of opoca): 1 - mixed with water and steamed; 2 - mixed with extract 2 and steamed; 3 - non-hydrated binding material.

The aim of the third stage of our work was to determine the influence of the specific surface (the grinding degree) of opoca on CaO binding rate and pozzolanic activity and to investigate the dependence of adsorption ability 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.

Data on the 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

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

Time (days)	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

The influence of opoca specific surface area on the binding rate of CaO was not constant (table 6).

At the initial stage of the experiment (till 8 days) the largest opoca fraction (230 m²/kg) bound CaO by 20-25 % less than the smallest (1125 m²/kg). Later this difference grew up and after 30 days reached almost 50 %.

At the same time the pozzolanic activity (binding of CaO during a month (15 titration)) of opoca of different specific surface area was investigated (figure 5), because the references refer only to data of samples obtained through a 80 μm sieve. Pozzolanic activity greatly depends on the specific surface area of opoca.

Equation $y = 15.2 x^{0.41}$ most optimally describes the dependence of pozzolanic activity y of opoca upon its specific surface area x .

Different fractions of opoca were poured with a glucose (the main carbohydrate in extracts of different wood species) solution at a concentration of 0.3 % and the dependence of its adsorption ability upon particle fineness was investigated. The mixture in some intervals of time was stirred. After 2 and 24 hours the remaining concentration of glucose was determined by the method of iodometric adsorption. The initial level of

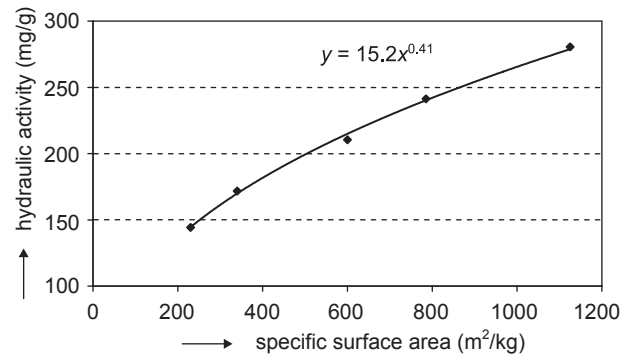


Figure 5. Influence of opoca specific surface on its pozzolanic activity.

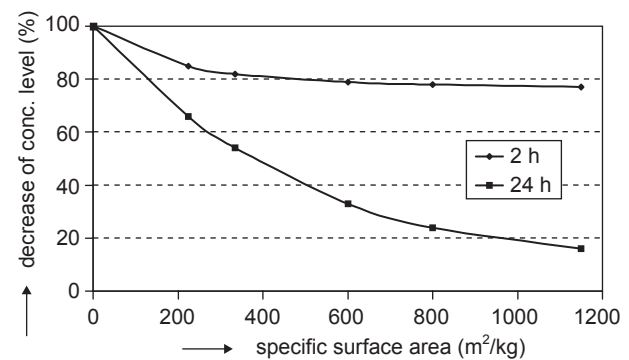


Figure 6. Change of 0.3 % glucose solution concentration after 2 and 24 hours of adsorption with an opoca of different specific surface area.

glucose solution concentration was equated to 100 %. The data on glucose concentration level after 2 and 24 hours of adsorption with an opoca of different specific surface area are presented in figure 6.

The data showed that at the initial stages of hardening of cement sawdust concrete, the biggest influence of particle fineness of the pozzolanic additive was exerted on the additive adsorption properties. Immediately after mixing of sawdust concrete with water, adsorption of separating wood extracts by the opoca began. From time to time a new proportion of extracts was separated, but at the same time its adsorption by the opoca intensified.

At the later stages of hardening, the influence of additive's particle fineness on the binding of separating $\text{Ca}(\text{OH})_2$ increased. It can be maintained that the higher fineness of the pozzolanic additive was the reason for the higher definitive compressive strength of concrete.

CONCLUSION

1. An alkali medium dissolves much more wood extractives than water. Under the influence of $\text{Ca}(\text{OH})_2$ hemicellulose disintegrates into soluble sugars.
2. Sugars retard the hydration of Portland cement.
3. Cement hydration, setting and hardening depend on wood extract concentration and don't depend on wood species and preparation method.
4. Addition of pozzolanic mineral materials, e.g., opoca, to cement mixtures decreases the harmful retarding effect of wood extractives. Because the specific surface of pozzolanic additives is much bigger than of cement and the sorption ability of these materials is higher, adsorption of water-soluble wood materials first of all takes place on the surface of pozzolanic materials and the concentration of extracts decreases.
5. The amount of free lime bound by pozzolanic material is an indication of its pozzolanic activity. This property depends greatly on the specific surface area of pozzolana. The influence of opoca specific surface area on the binding rate of CaO varies with time.
6. The most optimal equation to describe the dependence of opoca pozzolanic activity (y) on its specific surface area (x) is $y = 15.2x^{0.41}$.
7. At the initial stages of cement hardening the biggest influence of particle fineness of opoca additive is exerted on its adsorption properties.
8. At later stages of hardening, the influence of opoca additive particle fineness on its pozzolanic properties (binding of separating $\text{Ca}(\text{OH})_2$) increases.

References

1. Chittenden A. E.: Proceedings 7th World Forestry Congress, p. 6128 6134, Buenos Aires, 1972.
2. Simatupang M. H., Schwarz G. H., Broker F. W. : Proceedings 8th World Forestry Congress, p. 717 728, Jakarta, 1977.

3. Hon David N.-S., Shiraishi Nobuo: *Wood and cellulosic chemistry*, 2nd ed., p. 914, Marcel Dekker, Inc., New York, 2001.
4. Coutts R.S.P., Kightly P.: *J.Mater.Sci.* 19, 3355 (1984).
5. Pehanich J. L., Blankenhorn P. R., Silsbee M. R.: *Cement and Concrete Research* 34, 59 (2004).
6. Hachmi M. H., Moslemi M. A.: *Forest Products Journal* 39, 55 (1989).
7. Zhengtian L., Moslemi A. A.: *Forest Products Journal* 36, 53 (1986).
8. Thomas N. L., Birchall J. D.: *Cement and Concrete Research* 13, 830 (1983).
9. Bilba K., Arsene M-A., Ouensanga A.: *Cement and Concrete Composites* 25, 91 (2003).
10. Janusa M. A., Champagne C. A., Fanguy J. C. et al.: *Microchemical Journal* 65, 255 (2000).
11. Shcherbakov A. S.: PhD. Thesis, Moscow, 1984 (in Russian).
12. Biricik H., Akoz F., Berkday I. I., Tulgar A. N.: *Cement and Concrete Research* 29, 637 (1999).
13. Young J. F.: *Cement and Concrete Research* 2, 415 (1972).
14. Milestone N.B.: *J.Am.Ceram.Soc.* 62, 321 (1979).
15. Nanazashvili I.Ch.: Building materials of wood cement composition, p. 415, Strojizdat, Leningrad 1990 (in Russian).
16. Juenger M. C. G., Jennings H. M.: *Cement and Concrete Research* 32, 393 (2002).
17. Murthy C.: *Inter. J. for Housing Science and its Applications* 9, 313 (1985).
18. Vaickelionis G., Martusevicius M., Vektaris B.: *Chemical Technology* 2, 54 (1997) (in Lithuanian).

HYDRATAČE CEMENTU ZA PŘÍTOMNOSTI DŘEVNÍCH EXTRAKTŮ A PUCOLÁNOVÝCH MINERÁLNÍCH PŘÍRAD

GIEDRIUS VAICKELIONIS, RITA VAICKELIONIENE

*Faculty of Chemical Technology,
Kaunas University of Technology
Radvilenu str. 19, 50254 Kaunas, Litva*

V této práci byla zkoumána schopnost snižování škodlivého vlivu dřevních extraktů za přítomnosti pucolánových minerálních přísad a karbonátové opoky. Byl zkoumán vliv různých druhů dřevních extraktů na dobu a průběh tuhnutí dvou typů portlandského cementu - CEM I 42.5 R a CEM II/A-L 32.5. Bylo zjištěno, že hydratace cementu a jeho tuhnutí závisí na koncentraci dřevního extraktu a nezávisí na druhu dřeva a způsobu jejich přípravy. Vliv extrahovatelných přísad na pojivový materiál (čistý cement a cement s přísadou opoky) byl posuzován podle doby tuhnutí pasty pojivového materiálu, aktivního podílu reakčních produktů při hydratačních změnách cementu, pevnosti cementového kamene a rentgenové difrakce ztuhlého cementového kamene. Výsledky výzkumu ukazují, že dřevní extrakty snižují hydrataci cementu a pucolánové přísady tento vliv účinně zmenšují. Byla potvrzena vhodnost použitých minerálních přísad (opoka) s velkým specifickým povrchem a dále bylo zjištěno, že povrch opoky má vliv na vázání CaO . Specifický povrch opoky ovlivňuje jeho pucolánovou aktivitu a adsorpční schopnost. V počátečních fázích tuhnutí cementu byl pozorován nejsilnější vliv zrnitosti částic přísad opoky na její adsorpční vlastnosti. V pozdějších fázích tuhnutí se zvyšoval vliv zrnitosti částic přísad opoky na její pucolánové vlastnosti (vázání vylučovaného $\text{Ca}(\text{OH})_2$).