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**ARTÍCULO**

# Spruce chips stabilization in wood-cement materials: Effect of matrix composition

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**Abstract:**
The problem of the presented research is stabilization of spruce chips in modified cement matrix of wood-cement composites and analysing the effect of the stabilisation on selected parameters of these composite materials. The matrix has an impact on the stabilization of the spruce wood content. Silicate matrix based on Portland and blended cement was modified by finely ground thermal power plant slag (TPPS) and limestone (LS). Four types of wood-cement composite were subjected to water immersion tests for 28 days. During water immersion, both swelling in thickness and mass changes were analysed. The amount of sugars and pH in leachate were determined after 7 day intervals. Mechanical properties and microstructures were analysed before and after water immersion. Different behaviour with regard to spruce chips stabilization was proved in dependence of wood-cement matrix modification. Differences in thickness, swelling and sugar leach indirectly indicate the influence of the wood-cement composites matrix composition on the stabilization of spruce chips contained in this matrix. Boards with the matrix modified with thermal power plant slag showed the highest thickness swelling (%) and sugar leaching (0,042 %). Therefore, in the presence of thermal power plant slag modified matrix, spruce chips are more susceptible to sugar leach. The results of strength characteristics confirmed that sugars leached during hydration and after longer contact of wood-cement composites with water have no negative influence in their final properties in the case of all materials tested (reference and modified).

**Keywords:** Density, silicate matrix, spruce chips, swelling, wood-cement composite

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# Introduction

Wood-cement composite materials are widely used in the building industry. In actual construction, building materials are always in contact with humidity and water. Cement bonded composite materials with wood chips exposed to humidity are subjected to changes of physical or chemical properties (Amiandamhen and Izekor 2013).

During the manufacturing process of composite materials combining cement matrix and wood matter, the properties of the wood substance are stabilised. Stabilisation of wood is important for behaviour when humidity changes. Many scientists investigated the possibilities of wood stabilising and analysed the influence of $Al_2(SO_4)_3$, $Na_2SiO_3$, $CaCl_2$, $MgCl_2$, CaO, $FeCl_3$, $Ca(OH)_2$, $AlCl_3$, NaOH, $Al_2(SO_4)_3.18H_2O$ and cement (Bederina *et al.* 2012, Fan *et al.* 2012, Kochova *et al.* 2020, Nasser *et al.* 2016, Quiroga *et al.* 2016, Soroushian *et al.* 2013, Vasubabu *et al.* 2018, Wang *et al.* 2016).

As a considerable proportion of wood is present in the form of chips, the possibility of decomposition must be considered, releasing certain substances and chemical compounds from the wood material into the cement matrix. The leaching of hemicellulose could be problematic. An unproblematic amount of hemicellulose in wood before application into cement matrix would not exceed 0,5 % (Schwarz 1989, Sudin and Swamy 2006). This can be achieved, for example, by appropriate treatment such as ageing. A portion of hemicelluloses in wood is water soluble even at room temperature (Casebier *et al.* 1969, Örså *et al.* 1997, Willför and Holmbom 2004, Azhar *et al.* 2015). The solubility of hemicelluloses is affected by fact that lignin crosslinks the different polysaccharides (Azhar *et al.* 2015, Lawoko *et al.* 2006). Another possibility is using additives, which contribute to the stabilization of properties and structure of wood. This is because the presence of hemicellulose in the hydrating matrix changes the reaction of $C_3A$ (tricalciumaluminate $Ca_3Al_2O_6$), which is the fastest reacting component of cement. Extraction components contained in wood particles may also be absorbed on cores of calcium hydroxide. For this reason, they slow down hydration of $C_3S$ (tricalcium silicate $Ca_3SiO_5$; (Bentz *et al.* 1994, Young 1972). Inhibiting components (i.e. including hemicellulose, sugars respectively) act such that an impermeable film is created around the non-hydrated grains of cement. In this manner, subsequently, the formation of calcium-hydro-silicates (C-S-H) and Portlandite (CH) is slowed (Fan *et al.* 2012, Quiroga *et al.* 2016).

Analysis of wood-cement composite materials with respect to modification of their composition with alternative raw materials is necessary, because it is possible to stabilize wood in these composite materials not only by additions (soluble glass, sulphates, chlorides), but also by the composition of the matrix. The composition of cement influences the final mechanical properties of wood-cement composites with respect to the compatibility of matrix and wood (Schwarz and Simatupang 1983, Schubert *et al.* 1990). It was proven that molecules based on Ca or Si diffuse into the cellular structure of wood chips (Parameswaran *et al.*1977). Crystalline components of the matrix penetrate into the structure of wood material where lumens and medullary rays are partly filled with these hydration products (Dewitz *et al.* 1984).

The aim of this study was to indirectly verify the stabilization of properties of spruce chips in wood-cement composites placed in water for 28 days. Intention of the research presented was also assessing the physical and mechanical parameters of the composite materials (i.e. density, strength, elasticity modulus and thickness swelling). Another important aim of the study was an analysis of sugar content in the water baths where boards were placed.

# Materials and methods

## Mixtures and raw materials

The reference mix-design for analysed materials consists of 18 % wood in the form of spruce wood chips (size 0 mm to 8 mm, ca. 30 % particles from 1 mm to 2 mm; for details see Melichar *et al.* (2021a), 50 % cement (Portland or blended), 30 % water and 2 % hydration additions, each of which represents composition by weight. Two modified mix-designs were proposed. Their composition was modified by alternative raw materials.

As regards composition, the materials are highly compatible with the original matrix. The modification of the composition of mix-designs was also realized with respect to previous research results (Melichar *et al.* 2021). The proposed mix-designs are stated in the Table 1 below. Depending on manufacturing conditions, two types of cement are used for the manufacture of wood-chip cement boards. However, CEM II/A-S 42.5 R (from the

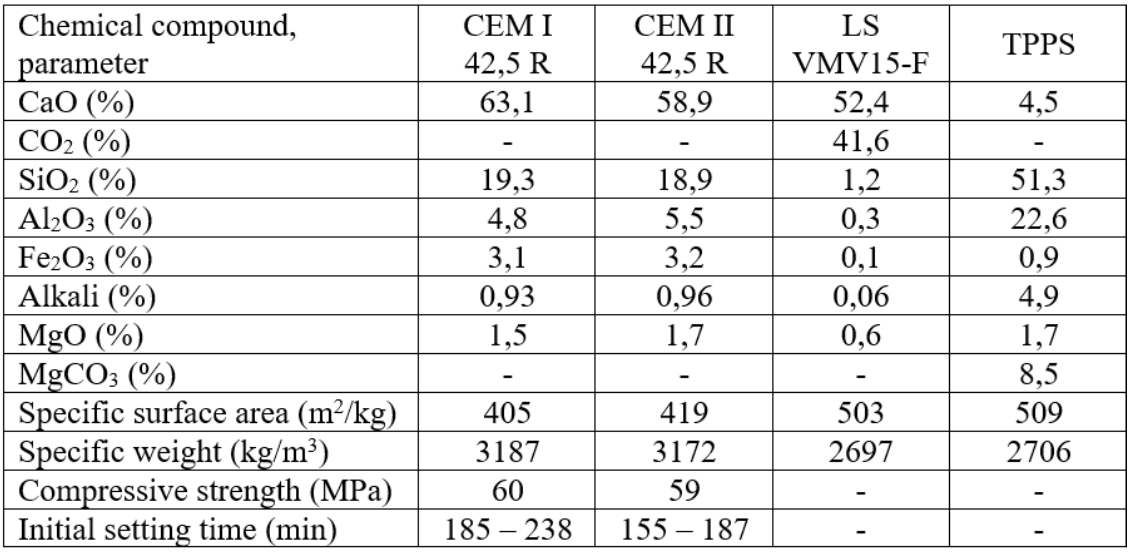
Company CIDEM Hranice, a.s.) is used more frequently. For this reason, modification of the matrix with CEM II was carried out.

Thermal power plant slag (TPPS) and limestone (LS) were selected as alternative components for the matrix, where these two (in particular LS) could positively contribute to the formation of the matrix-structure of wood-cement composites. A detailed analyses of alternative components LS and TPPS are presented in (Melichar *et al.* 2020). TPPS was formed during the combustion process of bituminous coal in the thermal power plant in Oslavany, which produced electricity until 1993. Some 850 thousand tons of TPPS remained in the closed area of former thermal power plant in Oslavany. The properties of the cements, TPPS and LS used are presented in Table 2. Figure 1 shows the particle size distribution of the raw materials.

**Table 1:** Composition (mass %) of designed mixtures – both reference and as modified by LS and TPPS.

| Component | Designed Mixtures / Composition in % | | | |
|---|---|---|---|---|
| | C-I | C-II | C-IIL | C-IIS |
| CEM I 42.5 R | 50 | 50 | – | – |
| CEM II A/S 42.5 R | – | – | 45 | 45 |
| Limestone (LS) | – | – | 5 | – |
| Slag (TPPS) | – | – | – | 5 |
| Spruce chips | 18 | 18 | 18 | 18 |
| Water | 30 | 30 | 30 | 30 |
| Admixtures | 2 | 2 | 2 | 2 |

**Table 2:** Properties of the cement CEM I 42,5 R, CEM II 42,5 R, LS VMV15-F and TPPS.



| Chemical compound, parameter | CEM I 42,5 R | CEM II 42,5 R | LS VMV15-F | TPPS |
|---|---|---|---|---|
| CaO (%) | 63,1 | 58,9 | 52,4 | 4,5 |
| $CO_2$ (%) | - | - | 41,6 | - |
| $SiO_2$ (%) | 19,3 | 18,9 | 1,2 | 51,3 |
| $Al_2O_3$ (%) | 4,8 | 5,5 | 0,3 | 22,6 |
| $Fe_2O_3$ (%) | 3,1 | 3,2 | 0,1 | 0,9 |
| Alkali (%) | 0,93 | 0,96 | 0,06 | 4,9 |
| MgO (%) | 1,5 | 1,7 | 0,6 | 1,7 |
| $MgCO_3$ (%) | - | - | - | 8,5 |
| Specific surface area ($m^2$/kg) | 405 | 419 | 503 | 509 |
| Specific weight (kg/$m^3$) | 3187 | 3172 | 2697 | 2706 |
| Compressive strength (MPa) | 60 | 59 | - | - |
| Initial setting time (min) | 185 – 238 | 155 – 187 | - | - |

CEM I 42,5 R – Portland cement, compressive strength 42,5 N/$mm^2$, rapid hardening. CEM II 42,5 R – Blended cement, compressive strength 42,5 N/$mm^2$, rapid hardening. LS VMV15-F – fine ground limestone (Kotouč Štramberk). TPPS – thermal power plant slag (Oslavany).

The major component in the crystalline phase of the LS Kotouč Štramberk VMV15-F is calcite, then aragonite, traces of magnesite and silica (quartz). The major component in the structure of the TPPS is the amorphous phase (85 %). Then quartz, hematite, mullite, spinel and magnesio ferrite are contained. Microstructure and element composition of TPPS shows Figure 2. Si and Al are dominant chemical elements contained in TPPS.

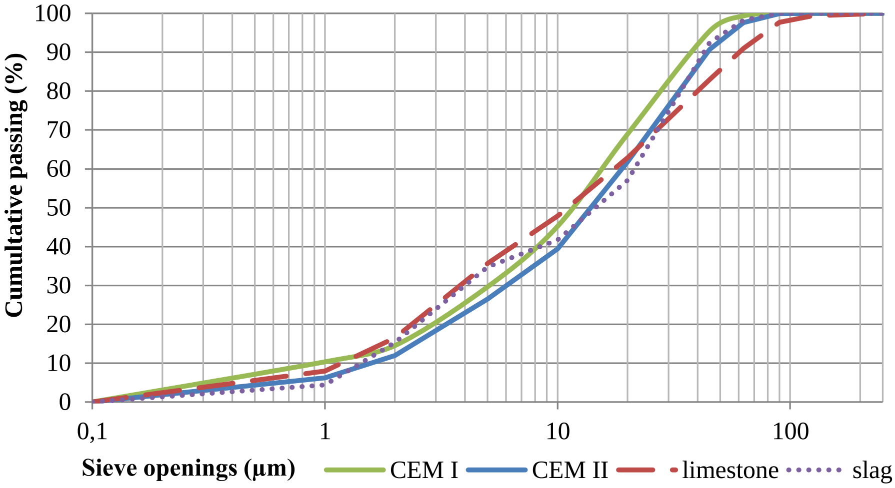
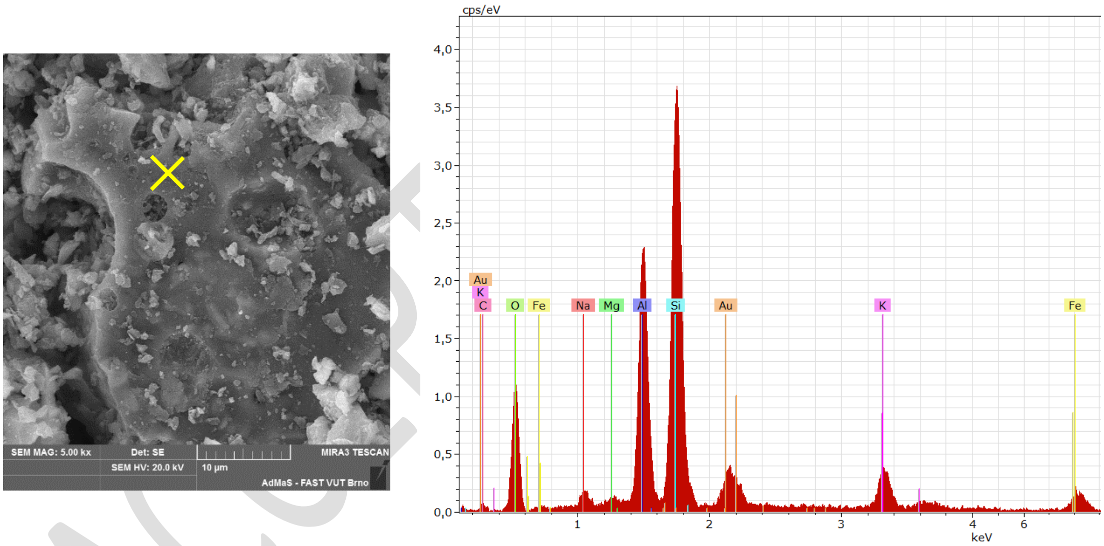


**Figure 1:** Cumulative particle size analysis of cement CEM I 42,5 R, CEM II/A-S 42,5 R, TPPS and LS VMV15-F.



(a) (b)

**Figure 2:** Microstructure of TPPS (a) SEM picture, (b) EDX analysis.

## Production of the wood-cement boards

Wood-cement composite materials containing spruce chips were used into boards with 12mmthickness. These boards were produced directly in the CIDEM Hranice, a.s. production facility (producer of the cement-bonded particleboards in the Czech Republic). Production was divided into 8 stages (Figure 3). All primary materials (cement, chips and admixtures) were automatically batched into the mix. Alternative materials (LS and TPPS) were manually added into the mix (Figure 4a).

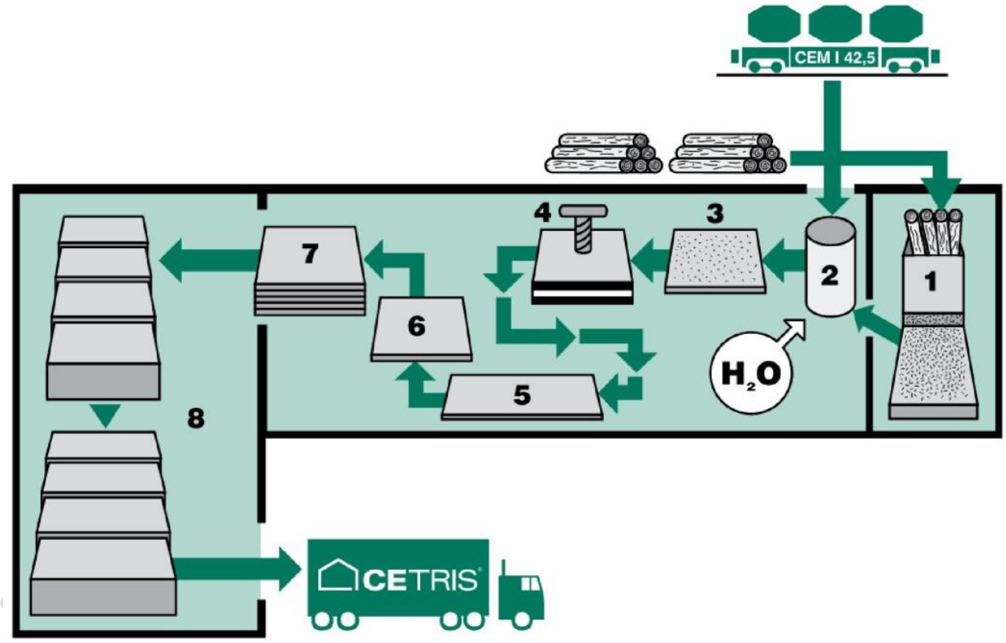


**Figure 3:** The production flow-chart of CIDEM Hranice, a.s. cement-bonded particleboard: 1 – spilling; 2 – preparation of mixture; 3 – layering of boards; 4 – pressing; 5 – drying; 6 – formatting; 7 – storage; 8 – transport (cetris.cz).

(a) (b)

**Figure 4:** (a) TPPS batching to the mix; (b) Detail of mixing the spruce chips in the production line of CIDEM Hranice, a.s.

After pressing, the boards were placed into a steaming chamber due to the acceleration of forming the compact structure of cement matrix. This process lasted ca. 8 hours at a temperature up to 50 °C. Then the boards were removed from the chamber and aged 7 days. Next step was drying (Figure 3 - stage 5) at a temperature of up to 80 °C. Further test specimens with various dimensions were made (Figure 3 – stage 6, formatting/cutting): 50 mm × 50 mm × 12 mm (for testing density, tensile strength perpendicular to the plane of the board and thickness swelling) and 290 mm × 50 mm × 12 mm (for testing bending strength and modulus of elasticity in bending).Test specimens were then transported to laboratories at the Brno University of Technology (Faculty of Civil Engineering). In the laboratory, half of these test specimens were subsequently saturated with water for 28 days after production at a temperature of 20 ºC ±2 °C.

# Sugars and pH analysing

If cement composites contain wood material, it is necessary to observe the possible release and deterioration of hemicellulose to monomers in the alkali environment (cement matrix). Free sugars contained in the sap of spruce are also important. The main sugar constituents of the hemicellulose in wood are D-glucose, D-mannose, D-galactose, D-xylose and L-arabinose (Sjöström 1993). The major hemicellulose in spruce is galactoglucomannan, which consists of a backbone of randomly distributed (1→4)-linked mannose and glucose units with side groups of (1→6)-linked galactose units attached to mannose (Azhar 2015, Sjöström 1993, Timell 1967). Not all types of sugar have the same inhibitory effect (Na *et al.* 2014). Glucose and sucrose were determined as the main inhibitory components for the hardening of cement matrixes (Yasuda *et al.* 2002). A small amount of hemicelluloses (0,1 %) significantly decreases the curing strength of cement and had a strong effect on cement matrix hydration. On the contrary, pentoses (xylose, arabinose) affect the hydration of cementto a lesser degree. (Miller and Moslemi 1991) Water-soluble hemicelluloses are hydrolysed (and converted) into carboxylic acid in an alkaline cement paste. Simultaneously, the alkaline degradation products are three times more efficient than wood extractives to inhibit the cement matrix hydration (Govin *et al.* 2005).

Thus, in the presence of wood, considerable retardation of chemical reaction of clinker materials may occur during formation of the structure of the cement matrix. Wood chips are usually mineralised (stabilised) with water, glass and aluminium sulphate during the manufacturing process (commercial production CIDEM Hranice, a.s.) to inhibit the release of sugars during maturing. Increasing the temperature to ca 45 °C) during the manufacturing process also helps stabilize the properties of wood (Yel *et al.* 2020). The content of hemicelluloses and free sugars in spruce chips was reduced by seasoning down to the amount of 0,24 %. However, it is still possible that these compounds can be released after longer contact with those wood chips contained in the cement matrix. Therefore, it was considered that sugars should possibly be extracted from the wood chips when placed in the water bath. For this reason, samples of water were taken after 7, 14, 21 and 28 days of the placement of test specimens. Samples of water were analysed to determine the content of sugar and the pH value. The content of sugar in the leachate was decreased by reduction of sugar with potassium permanganate ($KMnO_4$) in an alkali environment. Reductions from MnVI to MnIV are accompanied by colour changes of the solution to yellow or brownish yellow. At high concentration of permanganate, brown precipitates of $MnO_2$ can form. The pH value was determined with the Mettler Toledo apparatus (pH meter).

## Thickness swelling

Standard CEN EN 317 (1993) describes thickness swelling of a specimen after being completely immersed in water. Specimens with dimensions 50 mm × 50 mm × 12 mm were used. Each set contained 6 test specimens. Before swelling the samples were conditioned in a BINDER MKF 115 environmental chamber at 65 % ± 5 % relative humidity and 20 ºC ±2 °C until constant weight was reached. Test specimens were submerged into clean water with 7±1 pH and 20 ºC ± 1 °C. Before and after 1, 4, 6, 8 and 12 hours, followed by 1, 2, 3, 4, 7, 14, 21 and 28 days, specimens were removed from the water bath and both dimensions and weight determined. Thickness was measured at the intersection of diagonals with a KINEX 6040-15-200 digital calliper with an accuracy of 0,01 mm. Mass was obtained with a KERN PCB 1000-2 laboratory scales with readability of 0,01 g. Swelling of each specimen is determined by percentage comparison to the original (i.e. before immersion).

## Physical and mechanical tests

Before testing physical and mechanical properties, the wood-cement composites were placed in a BINDER MKF 115 environmental chamber at relative humidity (65 % ± 5 %) and (20 ºC ±2 ºC). Testing was carried out after reaching constant mass within this environment. The CEN EN 634-1 (2007) technical standard describes the requirements for further mentioned properties density CEN EN 323 (1993), bending characteristics CEN EN 310 (1993) and tensile strength CEN EN 319 (1993) were determined before and after placing in water baths.

Procedures for the aforementioned tests describe, among those standards mentioned, the study focused on the behaviour of cement-bonded particleboard with modified composition under static load press (Melichar *et al.* 2021b). In total, two sets of materials for each type of board were tested – 1 reference set and 1 set of test specimens, which were saturated with water and subsequently dried under laboratory conditions (the set, which was analysed for sugar leach). Each set consisted of 6 test specimens. The Testometric M350-20CT device was used for strength and modulus of elasticity testing.

### Microstructure

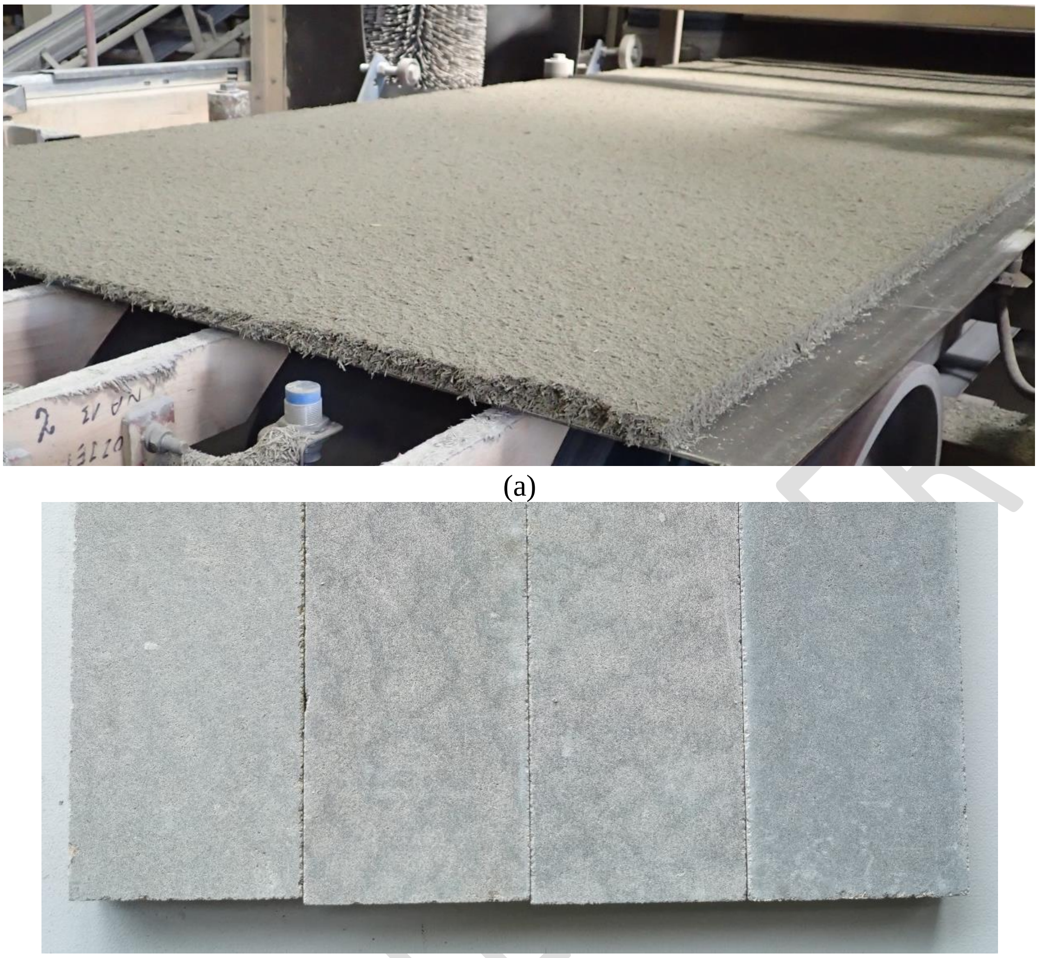
At the end of each 7-dayperiodof water immersion, the structure of wood-cement composites was analysed in detail with the Keyence VHX-950 Foptical microscope. Emphasis was placed upon volume changes of spruce chips in the cement matrix. A TESCAN MIRA3 XMU scanning electron microscope, with a 1,2 nm resolution at 30 kV was also used for analysis of microstructures with a focus on the contact zone of cement matrix and spruce chips. This emphasized the identification of products of the matrix in the cellular structure of spruce particles.

## Results and discussion

### Production of boards

No negative effects were found regarding the modification of cement-bonded particleboard production processes. The mixing achieved a required degree of homogeneity of the mixture, as was apparent from the fresh layered mixture (Figure 5a). All the following production steps, including pressing, steaming, handling, etc.,) were managed without complication and in accordance with regular technological processes.

The testing specimens were created from matured and dry boards, cut using a CNC machine. No anomalies or negative effects caused by the modified composition of the boards were found during this production phase. Only certain differences in color-tone were identified (Figure 5b), related to the characteristics of the alternative materials used (LS – white tone, TPPS – dark grey to black tone).

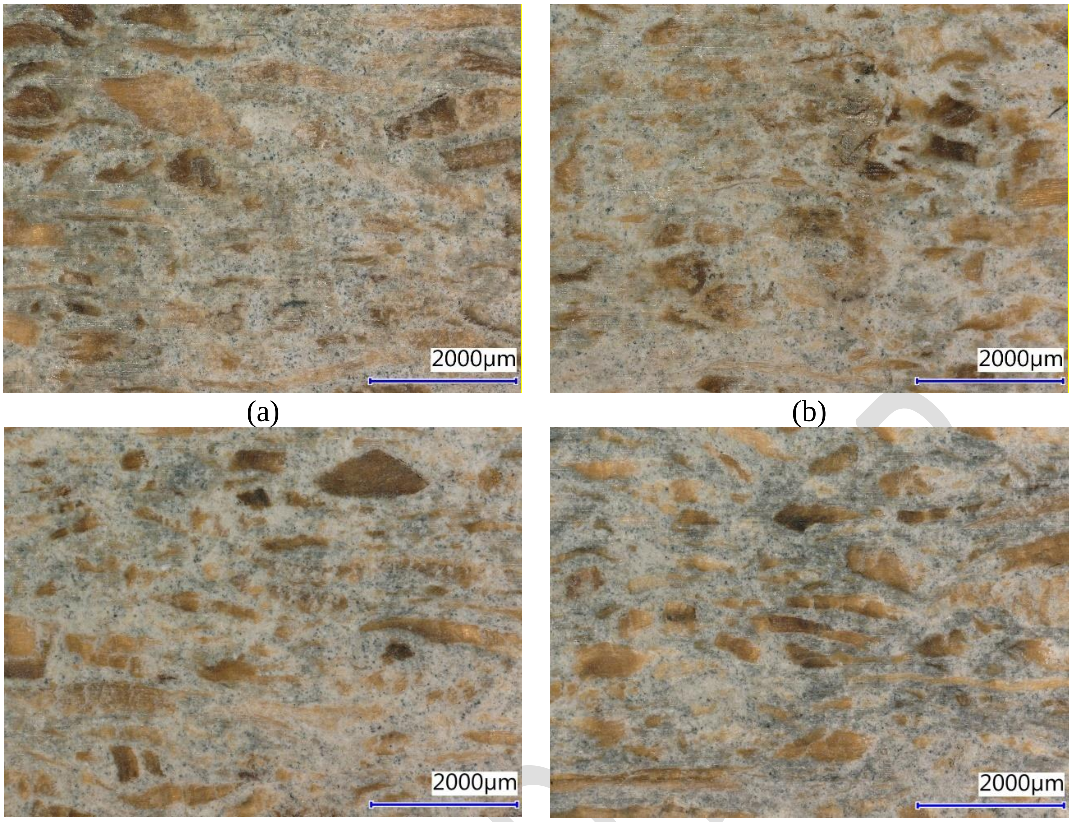


(a)

(b)

**Figure 5:** (a) Wood-cement mixture before pressing in the CIDEM production line CIDEM Hranice, a.s.; (b) Representative test specimens (from left) C-I, C-II, C-IIL and C-IIS.

The structure of test specimens is compact, without any discernable cracks, holes or pores, as is also evident from detailed images of the edges of the test specimens, obtained by an optical microscope (Figure 6).



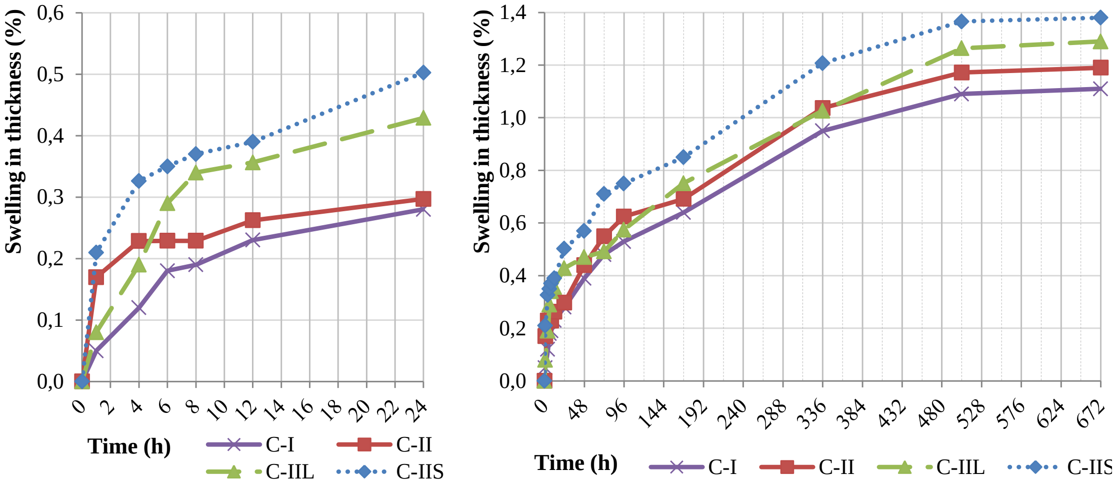
(a) (b)

(c) (d)

**Figure 6:** Structure of wood-cement boards produced (a) C-I; (b) C-II; (c) C-IIL and (d) C-IIS.

## Swelling in thickness

In accordance with CEN EN 634-2 (2007), the maximal permissible value of thickness swelling after 24 hours in water is 1,5 %, which was achieved with all analysed materials (Figure 7a). The best results showed reference material (based on Portland cement) C-I and materials C-II and C-IIL, with as welling of 1,19 %, and 1,29 % after 28 days placement in water.



(a) (b)

**Figure 7:** Swelling in thickness of tested wood-cement composites – (a) Detail up to 24 hours, (b) Whole monitored interval of immersion up to 28 days.

Modification of composition with TPPS caused a slight decrease of resistance to swelling in thickness – after 28 days 1,38 %. Materials C-I and C-IIL show very similar resistance to thickness swelling after immersion (Figure 7a). After 24 hours, more considerable differences between materials based on cement (C-I and C-II) and modified materials (C-IIL and C-IIS) were observed. However, these differences diminish in time (Figure 7b). This phenomenon is connected with the gradual stabilisation of the structure of spruce particles in the matrix, by adding Ca ions. Because spruce chips (without supplementary stabilisation) show large volumetric changes in contact with water, it is plausible to consider the influence of stabilization of wood chips in the matrix structure. Compared to the TPPS, it is evident that LS has a considerable positive effect. The trend of curves of thickness swelling of materials C-I, C-II and CII-L is quite similar. However, higher values are noticeable after 28 days swelling in the cases of the modified materials C-II, C-IIL and C-IIS. The difference between C-I and C-IIL is 0,18 % and between C-I and C-IIS 0,27 %. The application of TPPS probably has only an insignificant contribution to the stabilization properties of wood material in the structure of wood-cement composites. This is also proven by the results of Melichar *et al.* 2021a, where it is clear that finely ground TPPS can be mainly applied as inert filler.

A comparison of sugar leach (Table 3) and thickness swelling (Figure 7) implies only a partial relation of these two evaluated parameters. The reason is most probably the influence of modifications of the composition on formation of the structure of the matrix itself, rather than the stabilization of contained wood material, which can also have an effect on the volumetric stability of tested materials exposed to water.

## Sugars leaching, pH and mineralogy

Placing cement composites with the contents of wood material in water may cause leaching of sugars from wood chips. For this reason, samples of water were taken after 7, 14, 21 and 28 days of the placement of test specimens. The content of sugar in these samples was then determined. When the samples were taken, it was clear that the water had considerably changed its colour towards yellow. Sugars reduce the rate of hydration in cement matrix. Even low concentrations (0,03 % – 0,15 %) of sugar has a retarding influence on the beginning of setting and the strength of cement-based composites (Janusa *et al.* 2000).

The following (Table 3) shows an overview of determined values of sugar in water leachate. Each set of test specimens of one mix-design was separately placed in water.

**Table 3:** Amount of sugars and pH value in leach after 7, 14, 21 and 28 days of immersion in water.

| Mix-design / material | 7 days | | 14 days | | 21 days | | 28 days | |
|---|---|---|---|---|---|---|---|---|
| | Sugar (%) | pH | Sugar (%) | pH | Sugar (%) | pH | Sugar (%) | pH |
| C-I | 0,005 | 7,842 | 0,012 | 9,103 | 0,027 | 9,759 | 0,035 | 9,894 |
| C-II | 0,007 | 7,936 | 0,016 | 8,957 | 0,032 | 9,880 | 0,037 | 10,058 |
| C-IIL | 0,007 | 7,215 | 0,015 | 9,062 | 0,031 | 9,905 | 0,036 | 10,023 |
| C-IIS | 0,009 | 6,982 | 0,021 | 8,746 | 0,034 | 9,344 | 0,042 | 9,651 |

The results show very low amounts of leached sugar after immersion of composites in water for 7 and 14 days. This amount is insignificant and without impact on the hydration of cement. Slightly increased amounts of sugars in the leach were determined after immersion of materials in water for 21days. Materials C-I, C-II, C-IIL and C-IIS showed amounts of leached sugar slightly above the low limit (Janusa *et al.* 2000). The highest leached amountswere observed in C-IIS material (0,042 %). Amounts of sugar in water leachates correspond with the material composition. The results show slightly positive influences of micronized LS (C-IIL). On the other hand, slightly increased sugar leach was noticed in the case of material modified with TPPS (C-IIS).

With sugar leach, it is also important to consider the environment surrounding spruce chips. A considerably more alkali environment contributes to higher solubility of hemicellulose from wood material (Frybort *et al.* 2008, Miller 1991). For this reason, the values of pH were determined on samples of water (Table 3). pH values show slight coherence with determined amounts of sugars. However, a direct relation of pH with the amount of leached sugars with respect to the difference of composition of tested materials was not observed. pH is simultaneously affected by matrix (releasing ions – increasing pH) and sugars leaching (decreasing pH). Sugar leachate is characterized by a slight drop of pH in the range of 5,7-6,8 (Azhar *et al.* 2015) or 6,6 (Kochova *et al.* 2017). A more significant drop of pH (to 2,74) can occur under more accelerated conditions (Rissanen *et al.* 2022). A drop of pH during hemicellulose dissolution relates to the creation of mainly galacturonic and glucuronic acids (Willför *et al.* 2009).

Decomposition of hemicellulose (from spruce chips in wood-cement composites) had no significant effect on the pH values of leach (Table 3). Increasing trends of pH due to immersion time is obvious for all wood-cement composites tested (C-I to C-IIS).

Based on sugar amounts found in leachate, it was determined that hydration reactions in the cement matrix (of spruce-cement composites) might be slightly influenced after 21 or 28 days of water immersion. However, it must be mentioned that $C_3A$ reacts very rapidly during the formation of the cement matrix structures, in the order of tens of minutes. As a consequence, it can be assumed that the reaction of $C_3A$ is not influenced at the rate of sugar leachate determined in (Table 3). The possible influence of hydration on$C_3S$ is more probable. However, this clinker material also reacts quite quickly. If water is present, it is highly probable that $C_3S$ reacts faster than sufficient amounts of sugars can be leached to slow down its hydration. Moreover, the content of $C_3A$ and $C_3S$ was reduced in C-IIL and C-IIS materials with modified composition (10% substitution of cement).

For this reason, samples for XRD analysis of mineralogical composition focused on the formation of clinker materials (in particular $C_3S$ and $C_2S$) were taken from test specimens placed both under laboratory conditions as well as in water. Diffraction lines were identified corresponding with the presence of $C_3S$ and $C_2S$ (Figure 8) in the materials analysed.

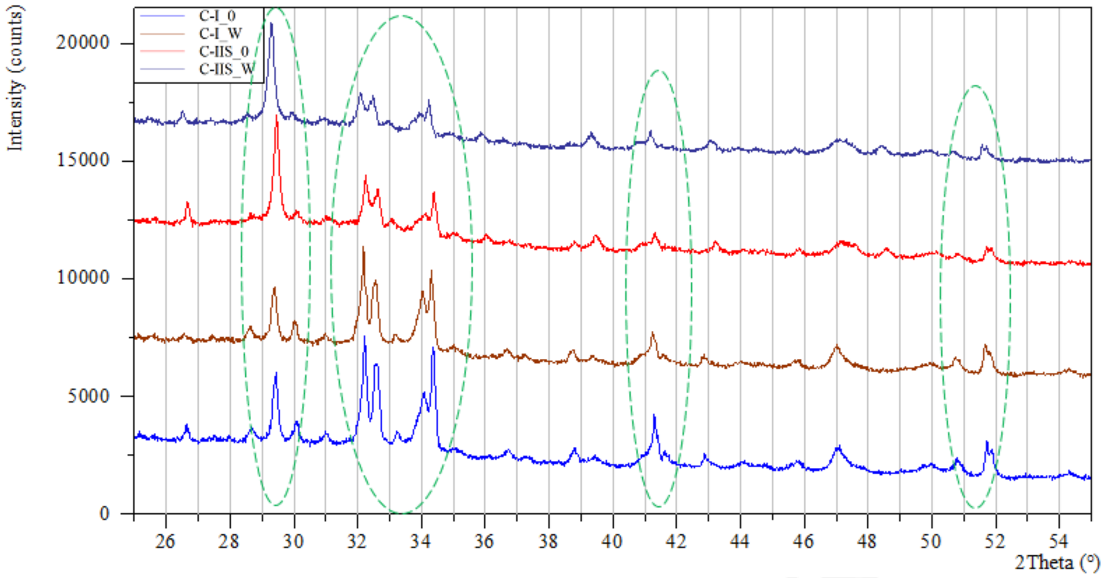


**Figure 8:** XRD results with emphasis on alite and belite (green areas in diagram) reference TPPS modified material before (C-I_0 – blue; C-IIS_0 – red) and after (C-I_W – brown, C-IIS_W – dark blue) water saturation.

In the case of $C_3S$ and $C_2S$, only minor differences were observed. Therefore, nothing indicates a different formation of cement matrix structure (hydration of alite and belite) due to sugar leach effects. A slight drop of peaks indicates ongoing hydration of alite and belite. It is evident that the amount of leached sugars can be found at the lower limit, i.e. with no possibility of influencing the reaction of clinker materials. Eventual retardation would be characterised by apparent differences in diffraction lines, which proved other authors (Vaickelionis and Vaickelioniene 2006, Pereira *et al.* 2006). The possible influence of sugars on hydration of cement matrix of tested materials was indirectly analysed as a part of the evaluation of strength and elasticity modulus.

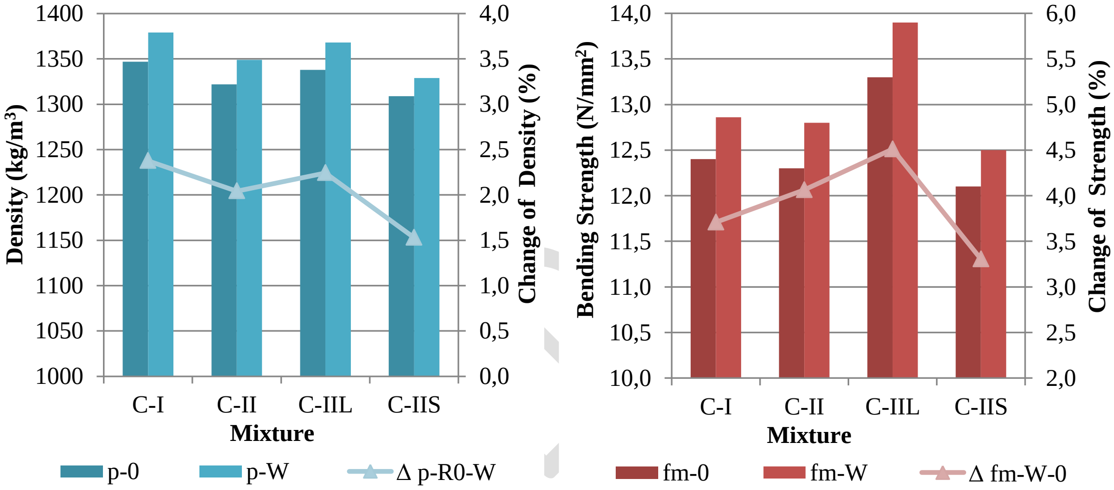
An interesting option for subsequent research is the use of fly ash (Cerny and Keprdova 2014) as a modifying component which may contribute to stabilising the structure of spruce chips in cement matrix.

## Mechanical parameters

In accordance with the requirements of the CEN EN 634-2 (2007) technical standard, the minimal value of density is 1000 kg/m$^3$. It is clear that all tested mix-designs have density > 1000 kg/m$^3$ (Figure 9a). The values of density of materials placed in standardized environments are from 1309 kg/m$^3$ to 1347 kg/m$^3$. Because of their immersion in water, the structure of test specimens became slightly more compact, and values of density increased from 1329 kg/m$^3$ to 1379 kg/m$^3$, which is a growth of 1,5 % to 2,4 %.

The results of determination of bending strength show a slightly positive influence of immersion in water and modification with LS (Figure 9b). In accordance with CEN EN 634-2 (2007), the minimal bending strength required is 9 N/mm$^2$. All tested versions of wood-cement materials conformed to this requirement. The values of bending strength of materials placed in standardized environments are from 12,1 N/mm$^2$ to 13,3 N/mm$^2$. Because of their immersion in water, values of strength increased by 12,5 N/mm$^2$ to 13,9 N/mm$^2$, which represents a growth in strength of 3,3 % to 4,5 %. It is interesting to find that materials with modified C-IIL composition show slightly higher strengths compared to reference mix-designs. It is evident that the modification of composition by LS is slightly advantageous. This finding is supported by the results of other authors, who state that micronized LS supports nucleation and the formation of crystals in cement matrix (Makhloufi *et al.* 2015, Oey *et al.* 2013).

The results of strength analysis confirm that sugars leached during immersion in water from chips have no impact in the ongoing hydration of cement matrix of materials analysed.



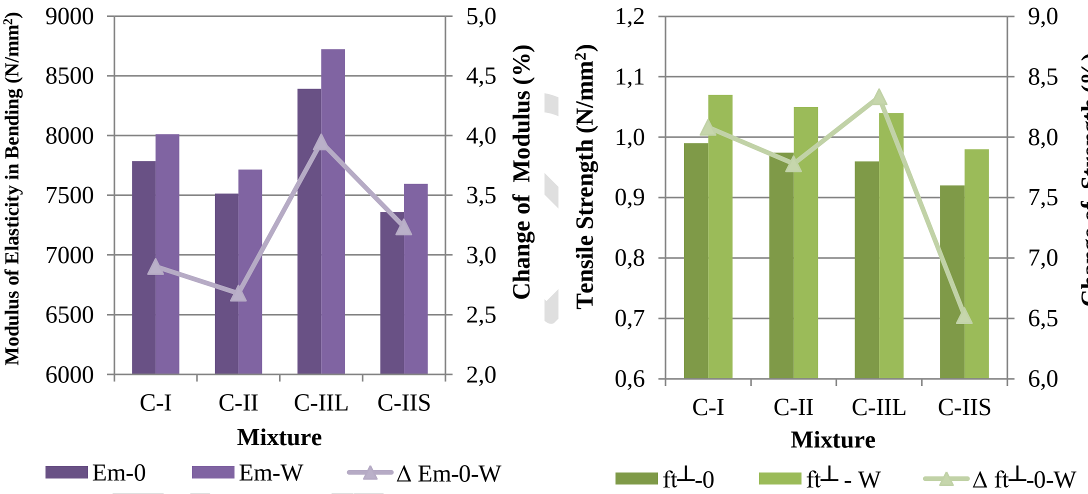
(a) (b)

**Figure 9:** (a) Density and (b) Bending strength of tested spruce-cement composites of modified composition.

As regards the values achieved of modulus of elasticity in bending (Figure 10a), the values tested are different than those of bending strength. Modified wood-cement composites (C-IIL and C-IIS) show growth of the modulus from 3,2 % to 3,9 %. On the other hand, materials based on Portland and blended cement (C-I and C-II) show an increase of the values of the modulus from 2,7 % to 7,9 % because of immersion in water.

With respect to the requirements of CEN EN 634-2 (2007), it is evident that all materials easily conform to the $E_m \geq 4500$ N/mm$^2$ requirement.

Tensile strength perpendicular to the plane of the board (Figure 10b) determines the cohesion of tested materials in the direction of compaction. In other words, this property shows strength in the direction of thickness. Wood-cement composite materials have varied properties in different directions. As regards the direction of thickness, the most marked changes of such materials are caused by humidity. For this reason, a determination of this tensile strength can be considered crucial.



(a) (b)

**Figure 10:** (a) Modulus of elasticity in the bending and (b) Tensile strengths of tested spruce-cement composites of modified composition.

In accordance with CEN EN 634-2 (2007), the minimal required value of tensile strength perpendicular to the plane of the board is 0,5 N/mm$^2$. All tested materials have average tensile strength $\geq 0{,}5$ N/mm$^2$ which is true even after immersion in water for 28 days. The results imply that the strength for all types of materials is on similar level, i.e. in the interval from 0,92 N/mm$^2$ to 0,99 N/mm$^2$, or from 0,98N/mm$^2$ to 1,07 N/mm$^2$ (specimens immersed in water).

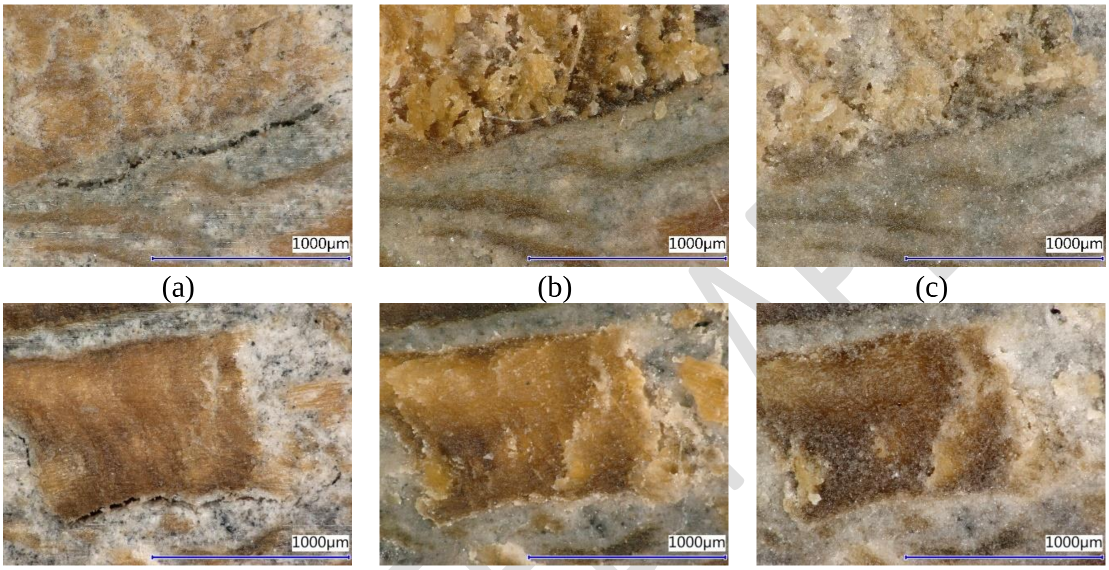
Specimens immersed in water show an increase of tensile strength from 6,5 % to 8,3 %. The positive effect of hydration on cement matrixes outweighed the retardation of hydration due to hemicellulose leach. The modification of cement matrixes with micronized LS (material C-IIL) again showed positive properties.

Considering all the results achieved and findings implies that the properties and structures of spruce wood in the form of chips were stabilized, which was confirmed by analysis of sugar leach and indirectly by an evaluation of the physical and mechanical properties of materials tested.

## Microstructure

In spite of the fact that spruce chips were mineralised, the images of the structure of wood-cement materials show that the dynamics of changes caused by the action of water is quite high. Images of the structure on the planes in the direction of thickness (Figure 11), in particular in the area of free hollows or cracks, show the encapsulation of these free areas in wood-cement composition, i.e. materials C-I and C-IIS. After encapsulation of all free hollows in the wood-cement composite, the spruce particles exert pressure on the surrounding matrix and this increases the volume of the composite material. Intentionally, images of both reference and modified materials are presented. These images clearly show that hollows are similarly closed in both reference and modified materials.

However, the pressure of spruce particles had a different effect, as well as coherence inthe matrix, which is not clear from the presented images (Figure 11) but from the results of thickness swelling (Figure 7).



(a) (b) (c)

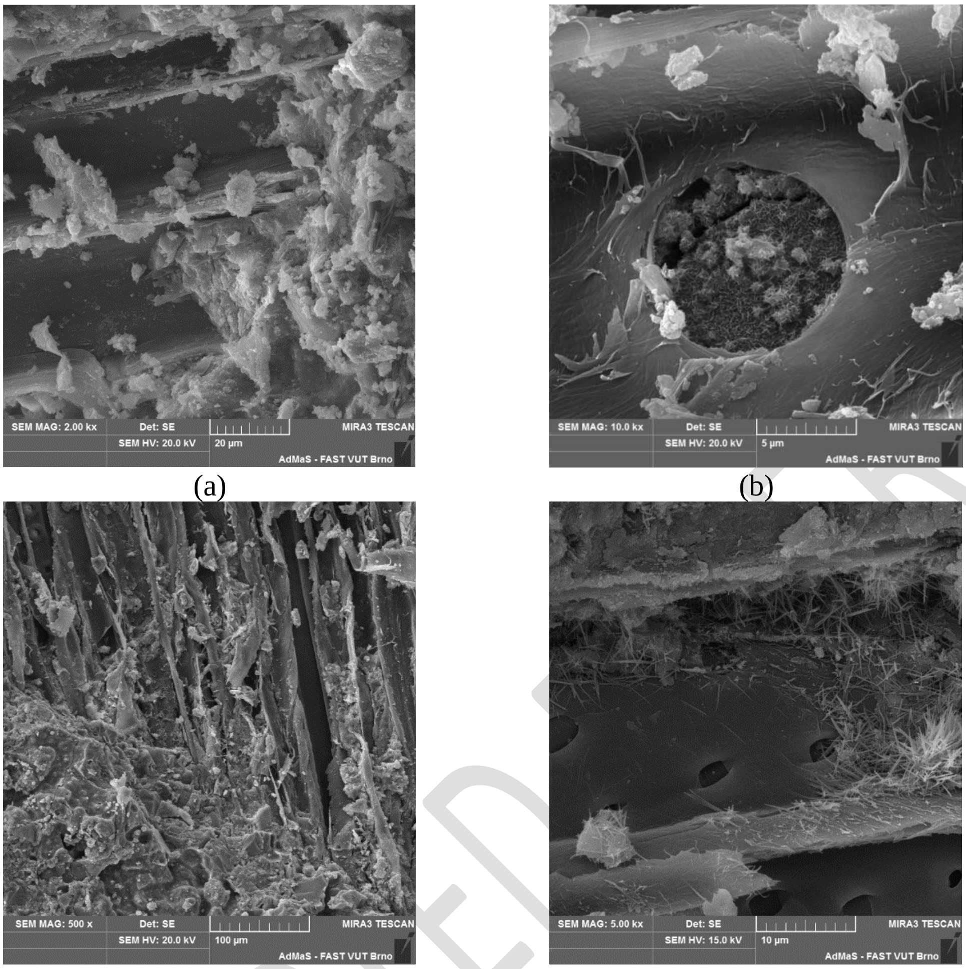
(d) (e) (f)

**Figure 11:** Microstructure of wood-cement material C-I – (a) Before and (b) After 4 hours, (c) 7 days of immersion; C-IIS – (d) Before and (e) After 4 hours, (f) 7 days of immersion (edge of the specimen, i.e. surface in the direction of thickness).

The microstructure of the wood-cement materials tested is compact and without apparent failures between the individual phases of the composite material. Both modification components of the matrix (LS and TPPS) act synergistically with hydration products. Micronized LS contributes more noticeably to the active formation of matrix structures. TPPS is, in this sense, a less suitable active substitute variant of cement binder.

The contact zones of cement matrix and spruce chips show no failures or defects, while the matrix products penetrate into the cellular structure of spruce particle (Figure 12). Penetration of reaction products into the spruce chips also confirm the findings of other authors (Caprai *et al.* 2018). It was proven that ions are exchanged between the wood material and cement matrix. This phenomenon contributes to improved anchoring of the matrix to the surface of wood chips (Frybort *et al*. 2008).

The development of interface and hydration products in cell structures (tracheids, lumens) were not negatively affected by sugars (hemicellulose) leached during water immersion. This thesis is supported by the findings of other authors (Wei *et al*. 2004), when the microstructure of analysed areas is similar. With respect to the stabilisation of spruce wood material in variously modified cement matrices, analysis of the microstructures show the suitability of alterative materials studied. All types of materials tested showed crystalline or amorphous phases of cement matrix, which considerably contributes to the stabilisation of properties and structures of spruce chips.



(a) (b)

(c) (d)

**Figure 12:** Microstructure of wood-cement composites –ITZ of (a) C-II and (c) C-IIL between matrix and spruce particles; detail of matrix products growing into the cell structure of spruce wood in (b) C-II and (d) C-IIL (samples immersed in water for 672 h).

# Conclusions

The experiments carried out presented findings concerning the behaviour of wood-cement composite materials with modified composition as regards the stabilisation of spruce chips contained in the cement matrix. Partial substitution of cement with alternative components with lower carbon footprints are advantageous from the ecological point of view.

Even though the properties of wood chips are stabilised during the manufacturing process of wood-cement composites, the leach of sugars related to decomposition of hemicellulose was observed. A slightly increased amount of sugar appears after 21 days of immersion in water. However, the determined values of leach were on the lower limit, which could possibly have a negative influence on hydration reactions.

Nevertheless, the results of strength characteristics indicate that sugars leached during hydration and after longer contact of wood-cement composites with water have no negative influence upon their final properties. The differences of mineralogical composition focused mainly on $C_3S$ and $C_2S$ (XRD) in wood-cement composites with regard to laboratory and water bath environments are negligible.

The mechanical properties of wood-cement composites were not negatively influenced. On the contrary, a slight increase of analysed parameters was observed, caused by immersion in water for 28 days. Ongoing hydration of cement had a more significant effect than the possible interference of the structure due to swelling of wood material contained in the matrix of tested materials. This finding applies to both reference and modified wood-cement composites.

The difference in thickness swelling of tested materials indirectly indicates the influence of composition of the matrix of wood-cement composites on the stabilisation of spruce chips contained in the matrix. Materials C-I, C-II and C-IIL (modified with LS) show similar swelling. C-IIS show a higher increase of thickness caused by immersion in water. This trend is, to a certain extent, also apparent for values of sugar leach, where the materials C-I, C-II and C-IIL have similar values, whereas C-IIS shows higher percentages of leached hemicellulose.

An analysis of microstructures proved the mineralisation and hence stabilisation of the cellular structure of spruce particles in all tested material variants of wood-cement composites.

Research presented in the article is limited to one type of environment (water bath). Therefore, in the scope of the future research, stabilised spruce wood in cement matrix shall be assessed with regard to hygroscopic behaviour and resistance to aggressive influences such as frost, sudden temperature changes, etc.

## Author contributions

T. M.: Conceptualization, methodology, validation, investigation, resources, writing—original draft preparation, writing—review and editing, visualization, supervision, project administration, funding acquisition. J. B.: Validation, data curation, Formal analysis, supervision. L. M.: Methodology, validation, investigation, resources. A. D.: Formal analysis, investigation. I. S.: Investigation, data curation.

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