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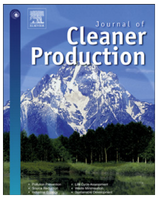

Ionic interaction and liquid absorption by wood in lignocellulose inorganic mineral binder composites

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ABSTRACT

This study investigates the suitability of alkali activated binders to replace Portland cement for lignocellulosic mineral-binder composite, aiming to lower the CO_2 footprint. The effects of wood composition on the reaction kinetics of the binders and the formation of the reaction products are studied using isothermal calorimetry and ion chromatography. The ionic behaviour analysis of Ca^{2+} and Na^{+} ions in the binders shows that in presence of wood, a neutralisation of OH^{-} ions and reduction of Ca^{2+} and Na^{+} ions during the first 24 h of curing take place, which alters the formation of C-A-S-H and N-A-S-H gels and influences the final composite performance. Moreover, the position of water absorbed by wood with different moisture levels is investigated by using T_2 relaxometry Time Domain (TD) NMR to understand the required water amount for the binder reaction as well as the liquid uptake of the wood and occurring ion migration. The results show that a hybrid binder consisting of 70% alkali activated material and 30% cement applied without NaOH pre-treatment results in a composite with excellent mechanical performances and reduced environmental impacts of 61.5% compared to a pure cement system.

1. Introduction

In the building sector, lignocellulosic-cement composites are popular products due to the appreciated properties of their constituents. The lignocelluloses in these composites are derived from naturally occurring terrestrial plants, available worldwide in large quantities, such as trees, bushes and grasses. Their lightweight porous structure makes them appropriate as a filler, providing thermal insulation and sound absorbing properties to the host composite (Ashori et al., 2011). Cement, on the other hand is applied as a binding agent, mineralizing the lignocellulose, resulting in high resistance to bio-degradation and fire (Jorge et al., 2004, Simatupang and Geimer, 1992). One example of a lignocellulose inorganic mineral binder product is wood wool cement board (WWCB) with favourable mechanical, thermal and acoustical properties, of which annually 16 million m^2 are applied in gyms, school buildings, parking garages (Doudart de la Grée et al., 2014a; Elten, 2015).

A common disadvantage of the lignocelluloses utilization is the inhibitory influence on the cement hydration (Fan et al., 2012; Wei et al., 2000a). The wood withdraws water from the surrounding cement paste and the leached soluble extractives from the wood interact with Ca^{2+} ions from the cement, forming complexation (Doudart De La Grée et al., 2017), which consequently influence the cement hydration kinetics. In case of WWCB, the external surface of the lignocellulose particles is mineralised with a layer of binder, in thickness of a few hundred μm while the wood wool is only about 500 μm thick. This indicates a potentially very large surface exposure, consequently high interaction potential (Doudart de la Grée et al., 2014a). Moreover, the produced boards have a high porosity of up to 85% with a density of ~325 kg/m^3 (Botterman et al., 2016). Hence, the migration of ions through the board occurs only locally. Moreover, for practical fabrication of this type of boards, the cement paste is expected to rapidly acquire sufficient strength to bind the lignocellulose particles. The inhibitory mechanism, which is very influential on composite properties, is still a studied matter especially when WWCB is concerned (Doudart De La Grée et al., 2017). Majority of available studies deal with the cement

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hardening applying methods including soaking of the lignocellulose, treatment with NaOH or addition of chlorides (Ashori et al., 2012; Pereira et al., 2006a). Nevertheless, those studies focus mostly on high density boards in which a low volume of wood or high content of binder is applied (Lee, 1991). Furthermore, a recent study (Caprai et al., 2018) focusing on calculating the water to binder ratio of the paste in presence of wood indicates how crucial a proper water to binder ratio is in order to successfully make wood wool cement composites.

The increasing worldwide awareness of the substantial contribution of Portland cement (PC) to greenhouse gas emissions (Florea et al., 2014; Ramezanianpour, 2014) promotes the search for alternative binding materials (Pacheco-Torgal et al., 2012, 2008; Provis, 2014). Replacement of cement by more sustainable alternative binders can lead to a reduction of the CO_2 footprint (Doudart De La Grée et al., 2018). As of today, supplementary cementitious materials like coal combustion fly ash or ground granulated blast furnace slag are already used as partial cement replacer, e.g. CEM II and CEM III (EN 197-1). Moreover, studies were performed on utilizing other sources of industrial by-products such as biomass fly ash, paper sludge fly ash and bottom ash (Caprai et al., 2017, Doudart De La Grée et al., 2018). However, the reaction kinetics of these alternative binders might differ substantially and requires deeper understandings. For instance, by increasing the substitution levels, the early strength development of the binders is drastically affected. Therefore, the addition of alkalis to enhance the dissolution of the supplementary materials has been introduced, allowing the full replacement of cement by providing fast activation and high strength development, while being more environmentally friendly. Moreover, because of their fast reaction and improved fire resistance compared to cement paste (Pacheco-Torgal et al., 2015), these so called alkali-activated materials seem to be beneficial for application in lignocellulosic composites.

Nonetheless, the combination of lignocellulose and an alkali-activated binder is not straightforward due to the desired alkaline conditions ($pH \approx 12-14$) required for the binder reaction, which is achieved by using activators such as NaOH, Na_2SiO_3, Na_2CO_3 or KOH, etc. However, the lignocellulose structure is prone to degrade under alkaline environment, leading to the increase of the water saturation point of the lignocellulose or changed lignocellulose microstructure (Tarkow and Feist William, 1969; Zabel and Morrell, 1992). Nevertheless, studies on the influence of alkaline binders on the lignocellulose are very limited although pre-treating lignocelluloses with alkali like NaOH to produce ethanol and biogas has been previously reported (Budzianowski, 2016). The treatment is known to involve several physical and chemical processes, e.g. dissolution of organic acids, polysaccharides, peeling reactions, hydrolysis of glycosidic bonds and acyl groups (Mirahmadi et al., 2010). Therefore, it is hypothesized that a treatment of the lignocellulose is possibly needed when utilized with an alkali activated binder (AAB), taking into account the consumption of alkali by the lignocellulose during the early reaction that sustains a sufficient alkalinity for an alkaline binder to react in the early age. This has been very recently confirmed crucial for cement hydration (Caprai et al., 2018), and it is even more crucial for AAB since water is only a transport medium for ions which means that an excessive amount will only lead to a more porous binder, resulting in poor binding capacities to hold the lignocellulose particles together. Therefore, proper pre-treatment is needed depending on the design parameters.

This study aims to understand the interactions between lignocellulose and alkaline activated binders considering reaction time, inhibitory influence and alteration in reaction products and eventually design a lignocellulosic composite with a reduced environmental impact. Firstly the physical and chemical characterisations of the used mineral binders and lignocellulose particles in the form of wood wool strands are investigated. Then, the lignocellulose behaviour under alkaline conditions is evaluated by monitoring the pH and assessing the reactivity of the binders using an isothermal calorimeter. This provides insights on the required pH conditions and the reaction behaviour at early stage. Next, the reaction products are studied by tracking the ionic behaviour of Ca^{2+} and Na^{+} in the absence and presence of lignocellulose strands, applying ion-chromatography. Further, the presence and position of the absorbed liquid water in lignocellulose is studied using T_2 relaxometry NMR to identify the ideal amount of water to be applied. Finally, the resulting findings are validated by designing a lignocellulosic inorganic mineral-binder composite applying medium size wood wool particles as they are primarily used for this type of product development in practice.

2. Materials and methods

2.1. Materials

2.1.1. Mineral binders

The binders used here are: a commercial Portland cement CEM I 52.5 R White (OPC) (designated Binder 1) (supplied by ENCI/HeidelbergCement, the Netherlands) and a one part alkali activated binder (AAB) (designated Binder 2) (supplied by Van Gansewinkel Minerals, the Netherlands). This one part alkali activated binder consists of industrial by-products (e.g. waste and paper incineration fly ashes) that are mixed with alkalis that only requires water to activate. Further, an alkali activated ground granulated blast furnace slag (GGBFS) (supplied by ENCI/HeidelbergCement, the Netherlands) (AAS) is investigated as a second alkali activated binder (Binder 4), here the alkali activator is designed by mixing waterglass with NaOH to reach desired alkali content and Na_2O/SiO_2 ratio which is added to the GGBFS following a procedure presented elsewhere (Skorina and Tikhomirova, 2012).

In addition to these three sole binders, two hybrid binders are studied to provide an alternative to the alkali pre-treatment. The first hybrid binder is designed by mixing 30 wt.% of OPC (Binder 1) and 70 wt. % of the one part AAB (Binder 2), and designated Binder 3, which is determined from our preliminary study (Caprai, 2015). The second hybrid binder is designed by mixing 30 wt.% of OPC (Binder 1) and 70 wt. % of the alkali activated GGBFS (AAS) (Binder 4), and is named Binder 5.

2.1.2. Lignocellulose

The used lignocellulose in this study is Norway spruce wood wool strands (*Picea abies*). This wood wool (see Fig. 1), supplied by Knauf Insulation (the Netherlands), is commonly applied in wood wool cement boards, having a width of 2.0 mm, thickness of 0.24–0.35 mm and length of 250 mm. The influence of sugars and spruce on the hydration of Portland cement has been investigated and reported elsewhere (Doudart De La Grée et al., 2017). For the analyses in Sections 3.2 and 3.4, the wood wool strands are milled to wood flour (Fig. 1) with a particle size of smaller than 400 μm to increase the inhibitory effect by generating a larger contact area.

2.2. Methods

2.2.1. Characterisation of the investigated materials

The elemental composition of the mineral binders is determined by X-ray fluorescence (XRF), and the main cement phases are calculated by using the commonly applied the Bogue method (Crumbie et al., 2006; Shanahan and Zayed, 2007). The physical properties such as BET specific surface area, mean particle size and density are measured by using a Micrometrics Tristar II 3020 with

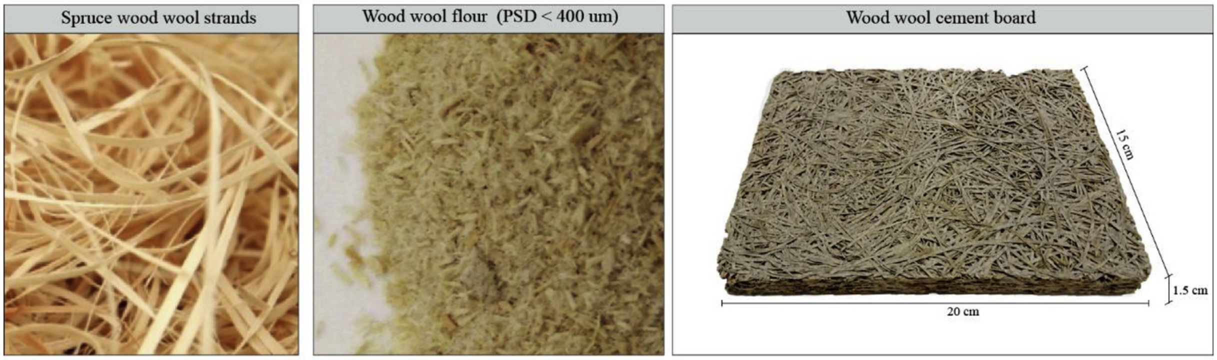


Fig. 1. Pictures of spruce wood wool strands, wood wool flour and wood wool cement boards.

N_2 adsorption, Malvern Mastersizer 2000 by means of the Fraunhofer approximation and an AccuPyc 1340 II gas Pycnometer, respectively. Detailed information regarding the measurement procedure of the involved instruments can be found elsewhere (Gao et al., 2017; Yuan et al., 2017).

The chemical composition of the wood is determined by using different techniques. The acid insoluble lignin is determined according to Tappi T222 and acid soluble lignin according to Tappi UM250 (Tappi Method T 222 om-88, 1988; Tappi Method UM 250, 1985). The extractives are determined according to Tappi T264 (Tappi T264 om-88, 1996). The polysaccharides, hemicelluloses and cellulose are determined by acid hydrolysis using a high performance anion exchange chromatograph.

The pore structure of the wood wool is determined by using a Mercury porosimetry AutoPorous IV 9500 from Micrometrics®. The microstructure of a strand covered without and with a binder is evaluated by using a Phoenix Nanotom® CT-scan. Furthermore, the morphology of the binder covered wood wool is also examined by using Scanning Electron Microscopy (SEM).

2.2.2. pH measurements

The pH behaviour in a time frame of 4 h is measured for 2 g of spruce wood in 80 ml of distilled water under the following alkaline conditions: NaOH concentration of 0.3156, 0.1000 and 0.0094 M corresponding to pH of 13.5, 13 and 12, respectively. Moreover, the pH behaviour of the binders 1–3 (i.e. CEM I 52.5 R white, one part alkali activated binder and hybrid binder comprised of CEM I 52.5 R white and one part alkali activated binder) in time is measured to specimens with a water to binder ratio of 0.5 and a binder to sand ratio of 0.3. At specific time intervals, 1 g of the specimen is taken and dissolved into 100 ml of distilled water of which the pH is measured.

2.2.3. Isothermal calorimetry measurement

The exothermic behaviour of the binder is monitored to evaluate its reaction kinetics. The heat release is measured using a TAM AIR isothermal calorimeter. The samples with a water to powder ratio of 0.5 are tested for 90 h under a constant temperature of 20 °C. The powder samples are first transferred in an ampoule and then water or alkaline solution is added. Subsequently, the mixture is well mixed before the ampoule is loaded into the isothermal calorimeter. The heat evolution data is calibrated by subtracting the heat evolution of ampoules with water as a baseline. Additional information regarding the used methodology can be found elsewhere (Gao et al., 2017).

2.2.4. Ionic analyses

The Ca^{2+} and Na^{+} ionic behaviour of Portland cement (Binder 1), alkali activated binders (Binder 2 and Binder 4) and hybrid binder (Binder 3 and Binder 5) are evaluated. The samples are prepared by first placing 0.2 g of wood powder in a beaker and in a separate beaker a paste by mixing a binder and water with the binder to water ratio by mass of 1.0. 2 g of the paste is taken after mixing for 2 min and added to the wood powder. The materials are then mixed until the wood powder is completely covered by the paste. At regular intervals, 10 g of water is added to the pre-mixed hardened paste and stirred until the paste is dissolved. The same procedure is followed for the pure mixtures without the wood powder.

The solution consisting of the paste is filtered through a 0.2 μm filter prior to analysis. The concentrations of sodium (Na^{+}) and calcium (Ca^{2+}) cations are analysed by using ion chromatography. A Dionex 1100 with ion exchange column CS12A (2 × 250 mm) with eluent 20 mM Methasulfonic acid with an isocratic flow of 0.25 ml/min is used. The determination of ions is carried out by suppressed (Dionex CSRS 300 2 mm) conductivity.

2.2.5. NMR analyses

The sensitivity of AAB to the amount of available water (diluting effect) (Nazari et al., 2014) and the occurring liquid uptake by the wood wool strands requires fundamental understanding (Wang et al., 2016). The liquid uptake by lignocellulose has been studied but remains complex due to the inhomogeneous microporous structure (Fourmentin et al., 2016; Siau, 1984). Therefore, the spin-lattice relaxation time of pre-wetted wood wool is measured by a T_2 relaxometry NMR at different moisture contents of 11, 50, 70 and 150%, respectively. Spin-echo decay curves are measured by the CPMG method using a 30 MHz Maran Ultra (Resonance Instruments Ltd, Witney, UK) TD NMR. A standard Carr-Purcell_Meiboom_Gill (CPMG) pulse sequence is applied. Per decay curve a total of 1024 echoes are acquired with an inter-echo time of 300 μs, 16 averages and a repetition time (TR) of 4 s. The data are analysed by a numerical inverse Laplace transformation, as implemented in CONTIN (Provencher, 1982), to get T_2-spectra that show the relative intensity as a function of the T_2-relaxation time. A high T_2 relaxation time corresponds to free water present in the large pores of wood (lumen) while a low relaxation time corresponds to water present in the narrow pores of the cell structure of the wood (cell wall). By this method, the amount of water can be determined to reduce the liquid uptake from the paste by the hygroscopic cell walls and lumens of the wood.

2.2.6. Lignocellulose mineral binder composite design

To validate the present findings, pre-treatment of wood wool and application of an alkali activated binder or hybrid binder are evaluated by creating a lignocellulose mineral binder composites with dimensions of 20 × 15 × 1.5 cm^3 (Fig. 1). The preparation procedure can be found elsewhere (Doudart de la Grée et al., 2014b).

Based on the obtained findings, boards are produced using two treatment routes to compensate the alkali consumption by: (1) Pre-treating the wood wool with an alkaline solution and applying the AABs (Binder 2 and Binder 4); (2) Pre-treating the wood wool with water, but applying a hybrid binder (Binder 3 and Binder 5) known as B4 and B5 in Table 1. Boards made from Portland cement (Binder 1) OPC is used as the reference (Table 1).

Further, tests are performed to Binder 3 to study the effect of wood to liquid amount, with a range between 3.45 and 1.97 (B6 - B8 in Table 1) which are examined using SEM. A complete overview of the boards is provided in Table 6. Although more properties such as sound absorption and fire resistance shall be evaluated, boards are considered to be satisfactory in the present study when a minimum flexural strength of 1.7 MPa is achieved after 10 days of curing with a target density of 400 kg/m^3 as both are practically primary parameters in relevant industry (Mencnarowski, 2014).

2.2.7. *Environmental impact*

The CO_2 footprints of the mixtures are evaluated in order to evaluate the sustainability of the created lignocellulose mineral binder composites. For this, values of CO_2 footprints per component of the binder and the activator are taken into account. These values are retrieved from available literature and data provided by van Gansewinkel as presented in Appendix Table A1 (Collins, 2010; Keulen, 2015; Turner and Collins, 2013).

3. Results and discussion

3.1. *Characterisation of the materials*

3.1.1. *Binders*

The chemical composition is shown in Table 2. By using the Bogue equations, the main cement phases of CEM I 52.5 R white cement (Binder 1) are computed. It is shown that this cement contains a high C_3A content of 10% and C_3S content of 80% compared to a CEM I 52.5 R (grey) of ~7% and ~56% (Doudart De La Grée et al., 2017), respectively as well as a similar gypsum content of approximately 3%. Moreover, this cement contains almost no C_4AF (negligible amount of 1%), in order to ensure the white appearance.

The one part alkali activated binder (Binder 2) contains a high amount of alkalis compared to the ground granulated blast furnace slag (Solid precursor in GGBFS), e.g. 0.73% K, 1.92% Na, 6.59% SO_3, which ensures that it can be activated with the addition of only water. Its SiO_2/Na_2O ratio of 12 is high, due to the presence of metakaolin derived from the incorporation of paper sludge fly ash, which also increases the CaO content (Mozaffari et al., 2009). The GGBFS (solid precursor in Binder 3) has a moderate content of CaO which is derived from $CaCO_3$ used in the calcination process during iron production (Pacheco-Torgal et al., 2008). Furthermore, it is rich in Si and Al, therefore, by activating with a NaOH modified Na_2SiO_3 activator, C-A-S-H gels are generated. The Na_2SiO_3 solution is composed of 27.69% SiO_2, 8.39% Na_2O and 63.9% H_2O by mass and together with NaOH leads to a high initial pH of ~13.2 and adjusted SiO_2/Na_2O ratio (Skorina and Tikhomirova, 2012). The physical properties of the binders are listed in Table 3.

An overview of the used mixtures and the 1 day compressive strength of the mortars made from these binders, following EN 196-1, are provided in Table 4. The results indicate proper reactions and mechanical strength properties in the absence of wood.

Binder 1 (Portland cement) is commonly applied in wood wool cement composites production due to its white appearance. Furthermore, high contents of C_3A and C_3S promote the early strength development of the binder (1 day compressive strength of 22 MPa, see Table 4), therefore supressing the inhibitory effects when mixing with lignocellulose. Binder 2 (one part AAB) is a one part alkali-activated binder consisting of industrial by-products. The binder reacts slower compared to Binder 1, leading to a 1 day compressive strength of 14 MPa. Nevertheless, Binder 2 is of interest since: (1) the reaction process is occurring at a low pH (~12.5); (2) it consists of minerals as a residue from the recycling industry. Binder 3 (hybrid of Binder 1 and Binder 2) is evaluated to enhance the activation of Binder 2 and stabilize the pH as will be explained in Section 3.2. After 1 day, a compressive strength of 17 MPa is achieved, which indicates the positive feature of this hybrid binder. Binder 4 is an alkali activated slag, achieving a high compressive strength of 30 MPa after 1 day (Gao et al., 2016; Pacheco-Torgal et al., 2008). Binder 5 (hybrid of Binder 1 and Binder 4) is evaluated to stabilize the pH as is the case for Binder 3 having a 1 day compressive strength of 27 MPa.

Table 1
Tested board recipes and evaluated wood to water ratios.

Sample	Binder		Water-to-binder ratio	Wood-to-binder ratio	NaOH/binder ratio	Na_2SiO_3/binder ratio	Wood-to p-retreatment liquid-ratio
	Name	Type					
B1	Binder 1	CEM I 52.5 R white (OPC)	0.50	0.75	–	–	2.30
B2	Binder 2	One part alkali activated binder (AAB)	0.50	0.75	0.1	–	2.30
B3	Binder 3	Hybrid OPC + AAB[a]	0.50	0.75	–	–	2.30
B4	Binder 4	Alkali activated GGBFS (AAS)	0.50	0.75	0.26	0.2	2.30
B5	Binder 5	Hybrid OPC + AAS[b]	0.50	0.75	0.035	0.14	2.30
B6	Binder 3	Hybrid OPC + AAB[a]	0.50	0.75	–	–	3.45
B7	Binder 3	Hybrid OPC + AAB[a]	0.50	0.75	–	–	2.30
B8	Binder 3	Hybrid OPC + AAB[a]	0.50	0.75	–	–	1.97

[a] This hybrid binder consist of 70% AAB and 30% OPC.
[b] This hybrid consist of 70% AAS and 30% OPC.

Table 2
Chemical composition of the applied materials [%].

Materials [%]	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3	MgO	TiO_2	Mn_3O_4	P_2O_5	Other oxides
CEM I 52.5 R white (Binder 1)	67.19	20.86	3.91	0.45	0.12	0.11	2.92	0.40	0.33	0.02	0.51	3.18
One part alkali activated binder (AAB) (Binder 2)	42.24	23.45	9.68	6.73	0.73	1.92	6.95	6.41	0.69	0.20	0.34	0.66
GGBFS (Solid precursor in Binder 4)	38.89	34.18	13.63	0.51	0.43	0.33	1.41	10.62	–	–	–	–

Table 3
BET specific surface areas, specific density (ρ_s) and the mean particle size of the used materials.

Binder	BET surface area [m^2/g]	ρ_s [g/cm^3]	D_{50} [μm]
CEM I 52.5 R white (OPC)	1.21	3.11	16.90
One part alkali activated binder (AAB)	3.67	2.92	25.00
GGBFS (Solid precursor in Binder 4)	1.70	2.89	30.00

3.1.2. *Wood wool strands*

The chemical composition of the wood wool strands is presented in Table 5. Monosaccharides usually have a pKa of 12 while the galacturonic and glucuronic acids have a pKa around 3.4, leading to neutralisation reactions in an alkaline environment (Kohn and Kovác, 1978; Rovio et al., 2007). The main component of the wood is cellulose, consisting of β(1 → 4) linked D-Glucopyranose units, having a polymerization degree of several hundreds to tens of thousands monomers (Chen, 2014). The second largest component is lignin, consisting mainly of Guaiacyl subunits, with a polymerization degree of a few thousands of monomers. Besides, there is a hemicellulose fraction consisting of several different polysaccharides (e.g. xylan and glucomannan) which are built up from sugar units like D-Xylose, D-Mannose, L-Arabinose, D-Galactose, and D-Glucuronic acid, often having a polymerization degree below 200 monomers (Chen, 2014). The presence of these monosaccharide units that are more prone to alkaline decomposition reactions are the cause of reducing the alkalinity of the system.

The wood wool is characterised by hexagonal shaped pores with a length of 120 μm and width of 40 μm, having a total porosity of 63%. The wood wool covered with and without binder is visualised elsewhere (Doudart de la Grée et al., 2014b). The thickness of this binder layer ranges between 40 and 140 μm (measured with the CT-scan) with a wood to binder ratio of 0.75 by mass. Therefore, the interaction between the wood wool and binder is magnified compared to a situation where the thickness of the binder layer (total binder volume) is much larger (e.g. millimetre range) like the case of boards where a higher binder dosage is used. Due to the high porosity and large surface area, the spruce wood wool strands is found to be very hygroscopic and is able to absorb liquid from the cement/water paste and swell (Fourmentin et al., 2016). This hygroscopic ability requires a proper pre-treatment, since subtracting liquid from the paste by the wood wool strands will have a negative effect on the reaction of the mineral binders. Moreover, the amount of liquid needs to be evaluated since AABs behave very differently under different alkali environments which is significantly affected by the water content (Fraay et al., 1989).

Table 5
Chemical composition of the used spruce wood wool strands in [%].

Compound	[%]
Cellulose	
Glucose	38.7
Hemicellulose	
Arabinose	1.3
Xylose	5.6
Rhamnose	0.4
Mannose	11.5
Galactose	2.6
Galacturonic acid	1.1
Glucuronic acid	1.9
Lignin (according to TAPPI T222 and TAPPI UM250)	
Acid insoluble lignin	25.4
Acid soluble lignin	0.2
Extractives (according to Tappi T264)	
Cyclohexane: Ethanol 2:1	1.8
Ethanol: Water 1:1	1.3
Water	1.6

3.2. *Behaviour of wood wool under alkaline conditions*

Fig. 2 shows the evolution of the pH of an alkaline medium containing wood wool strands over time. It is evident that wood wool leads to the reduction of the initial alkalinity (pH 13.5–12) by different mechanisms. In an alkaline environment the main wood components, presented in Appendix Table A2, can be degraded e.g. ester bond cleavage and peeling reactions (Sjöström, 1993, 1977), leading to smaller fragments of organic acids e.g. formic, acetic and hydroxyacids (see Appendix Table A2). The degradation of the reducing end-groups (peeling reaction) consumes OH^- (Loon and Glaus, 1997; Pavasars et al., 2003). Due to the lower polymerization degree and better solubility of hemicellulose in alkali compared to cellulose, these compounds are more susceptible to undergo the peeling reaction (Sjöström, 1993). Moreover, the formed acids neutralize the OH^-, leading to the formation of salts. The formed salts can precipitate and can form complexations, making the alkali ions unavailable for further reaction as binder (Thomas and Birchall, 1983; Young, 1972).

Within the 4 h testing time, the wood wool is able to neutralize 53% of the initial OH^- ions, reducing the pH from ~13 to ~12.6. This rapid reduction of OH^- concentration negatively influences the reaction of an alkali-activated binder, since most of the alkali-activated binders require a high concentration of OH^- ions to start the dissolution and maintain the reaction (Fraay et al., 1989). Therefore, a treatment is needed to compensate the OH^-

Table 4
Mortar recipes with compressive strength results.

Sample	Binder No.	Binder [g]	Water [g]	Sand [g]	NaOH [g]	Na_2SiO_3 [g]	1 day Compressive strength [MPa]
1	1	450	225	1350	–	–	22
2	2	450	225	1350	–	–	14
3	3	450	225	1350	–	–	17
4	4	450	168.3	1350	22.5	90	30
5	5	450	168.3	1350	15.75	63	27

Table 6
Overview of Mc, apparent density (ρ_b) and flexural strength of the evaluated boards.

Mix	Binder	Mc wood[a]	ρ_b [kg/m^3]	Flexural strength [MPa]
B1	CEM I 52.5 R white (OPC)	60	399	1.9
B2	One part alkali activated binder (AAB)	60	388	1.8
B3	Hybrid AAB + OPC	60	357	1.6
B4	Alkali activated GGBFS (AAS)	60	420	2.3
B5	Hybrid AAS + OPC	60	430	2.0
B6	Hybrid AAB + OPC	50	404	1.0
B7	Hybrid AAB + OPC	60	428	**3.1**
B8	Hybrid AAB + OPC	70	413	1.8

[a] Pre-treatment moisture content based on oven dry mass of the wood.

consumption to ensure that the AABs are able to react. This can be achieved by the addition of OH^- ions to the system. To compensate the pH reduction when wood is in contact with the binder, an equivalent amount of OH^- ions is added to the system to ensure the proper binder reaction, which will be further explained in Section 3.6.

3.3. Reaction kinetics of the binders

In Fig. 3, the pH behaviour and heat release of the mortars are presented to identify the OH^- behaviour and time period when the main reaction occurs. It is evident that the reaction kinetics of Binder 1–3 (Portland cement, one part AAB and hybrid of Portland cement and one part AAB) differ. Binder 1 maintains a stable pH of 12 in time (Fig. 3a), having a lower dissolution peak in the first 1 h compared to the other binders (Fig. 3b). The high pH is attributed to the fast dissolution of the cement phases C_3A, C_4AF and C_3S releasing Ca^{2+}, Al^{3+}, Fe^{3+} and OH^- ions (Doudart De La Grée et al., 2017). Afterwards a low reaction of the cement occurs up to 4 h (Fig. 3b and c), and the pH stays stabilized. After the induction period, the ions in the liquid start to form the hydration products (i.e. C-S-H and $Ca(OH)_2$) and the remaining phases continue to react, as observed by the continued liberation of heat.

Both Binder 2 and Binder 3 have initially a high pH because of the dissolution of alkalis releasing OH^- ions, as confirmed by Fig. 3b and c. After approximately 45 min, the pH starts to drop, due to the formation of reaction products which continues as long as the pH is higher than 9 (Pacheco-Torgal et al., 2015). It needs to be noted that the measured pH is not the real pH of the system since it is diluted and only used to observe the behaviour. The pH of Binder 3 remains constant (around 12) due to the implementation of 30% cement acting as a buffer. The heat release of Binder 3 compared to Binder 2 in the first 24 h is lower due to the presence of cement (liberates less heat in the first 15 h) but gradually liberates heat by formation of reaction products as seen for Binder 1 (Portland cement) presented in Fig. 3c.

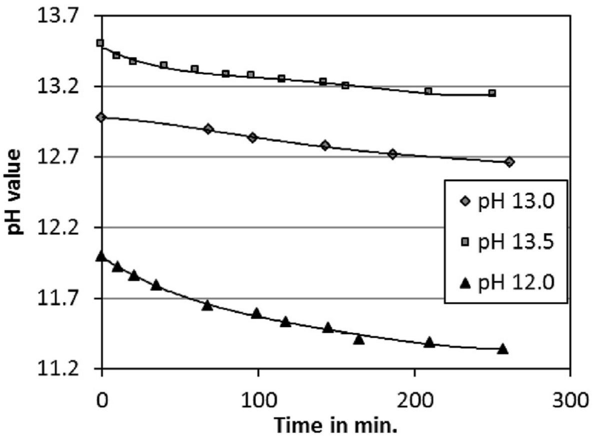


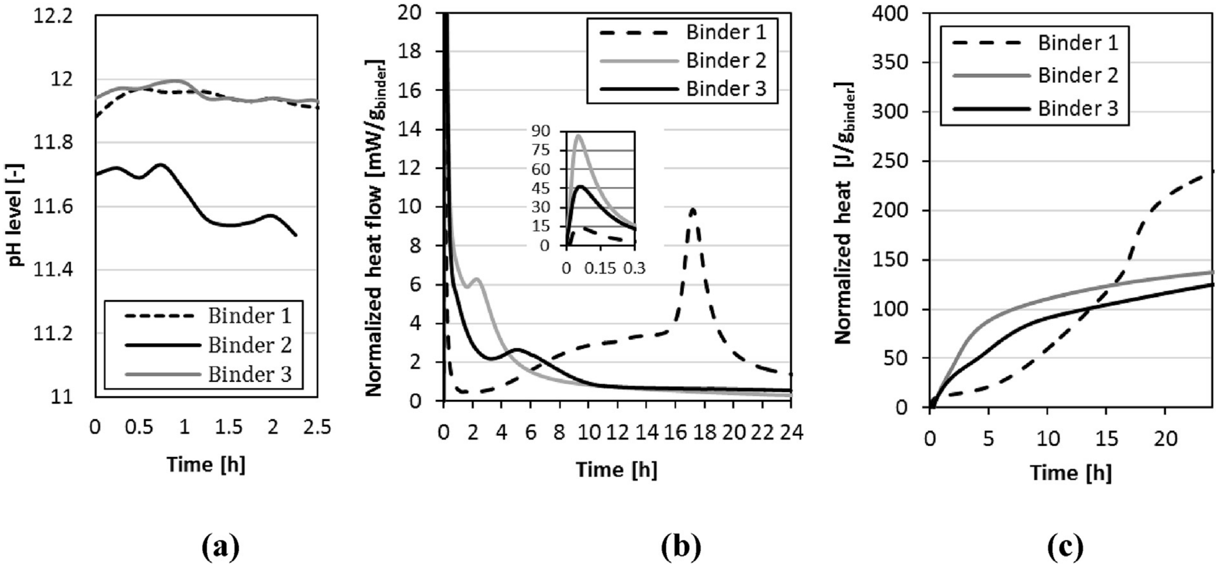
Fig. 2. pH behaviour of spruce wood wool strands under various starting pH conditions.

3.4. Ionic uptake of wood and alteration of binder reaction mechanism

As described in Sections 3.1 and 3.2, wood has the tendency to absorb ions from the cement paste, neutralizing the pH. This is investigated for Binders 1–3 on two cations Ca^{2+} and Na^+ using ion chromatography. The ion concentration in time (ionic behaviour) of Mix 1 (containing Binder 1) and Mix 2 (containing Binder 2) is shown in Fig. 4.

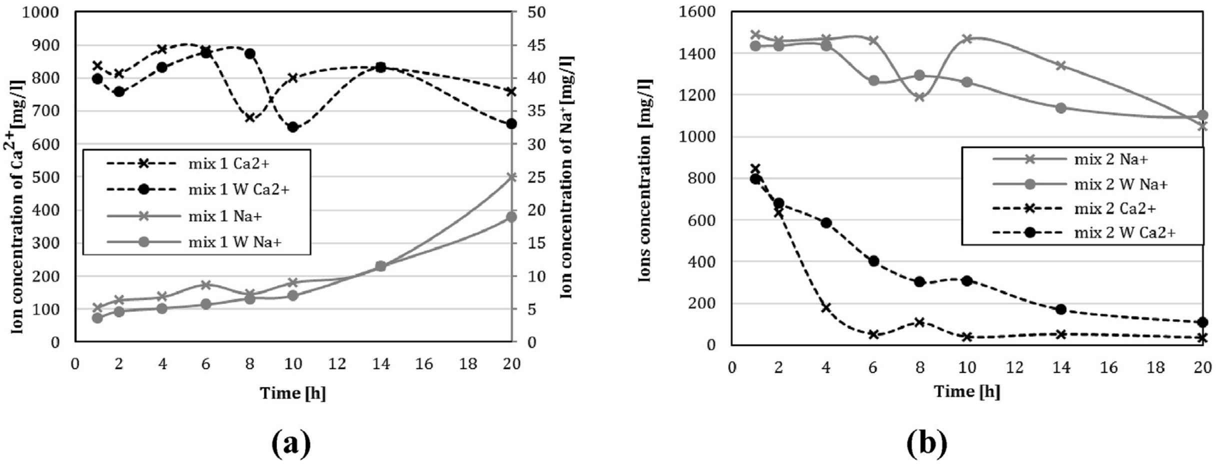
Fig. 4 displays the reduction of Ca^{2+}concentration by ~4.5% in Mix 1 W (with wood) compared to Mix 1 (without wood). This is in line with the study of Pereira et al. (2003) who described an initial adsorption of cations by wood resulting in a lower amount of initial Ca^{2+} ions in solution. In the period of 6–8 h Mix 1 shows a decrease in Ca^{2+} by 22.7%, which afterwards increases again. When the solution is saturated or supersaturated with respect to Ca^{2+}, precipitation of $Ca(OH)_2$ occurs, causing reduction of Ca^{2+} concentration in the liquid phase, while the continuous reaction of cement can increase the Ca^{2+} ions. The results are confirmed by Fierens and Verhaegen (1976), showing the precipitation of $Ca(OH)_2$ after 4 h of reaction up to 12 h, depending on the used C_3S amount present. However, other researchers described a slow decrease in concentration in the first 4 h (Rai et al., 2004; Singh et al., 1995). Therefore, the behaviour of Ca^{2+} ions is strongly related to the type of binder used and the concentration can differ based on the rate of dissolution of cement particles and interactions of Ca^{2+} ions with hydration products, leading to fluctuation of the Ca^{2+} concentration. Nevertheless, the postponed consumption of the Ca^{2+} in the presence of wood is clearly visible, occurring 2 h later (from 6 h to 8 h) compared to that of the pure mineral binder system. This indicates a delay in the reaction because the degradation of wood in alkaline environment leads to interactions between Ca^{2+} and degradation products (Bishop and Barron, 2006; Chen, 2014). The Na^+ concentration in Mix 1 with and without wood remains very low in the first 20 h because of the low content of Na^+ (0.11%) and only in time slowly increases, due to the further dissolution of cement.

For Mix 2 (without wood), a high initial concentration of both cations Na^+ and Ca^{2+} is observed, which declines at different rates. Again, the immobilization of ions when wood is present is obvious in the first hours and it is of the same magnitude as that of Mix 1. The results show a similar ionic behaviour in the first 2 h between Mix 2 and Mix 2 W (Mix 2 containing wood). In Mix 2, the Na^+ concentration starts to decline after 6 h but recovers at 8 h and then is slowly dropping, while the concentration of Ca^{2+} ions decreases



(a) (b) (c)

Fig. 3. (a) pH behaviour in time of Binders 1–3 (Portland cement, one part AAB and hybrid of Portland cement and one part AAB); (b) Normalized heat flow and (c) normalized heat of Binders 1–3.



(a) (b)

Fig. 4. Ionic behaviour of (a) Mix 1 (without wood) and Mix 1 W (containing wood) and (b) Mix 2 (without wood) and Mix 2 W (containing wood).

in the first 6 h and is afterwards only present in a very low amount. In the early reaction stage, with a high concentration of Ca^{2+} ions the formation of C-A-S–H gel occurs (García-Lodeiro et al., 2013). In time the pH drops and the amount of Ca^{2+} ions in the solution is reduced, allowing the formation of a secondary product in the form of N-A-S–H gel, which is favoured at a lower pH range (9–12) (Garcia-Lodeiro et al., 2015). In the presence of wood, the Na^+ concentrations are significantly lower after 4 h. On the other hand, the Ca^{2+} content after 2 h slightly declines, indicating that the formation of reaction products is occurring but in a much lower rate, influenced by the presence of the wood. The presence of wood affects the ionic behaviour in a higher degree than the case of Mix 1.

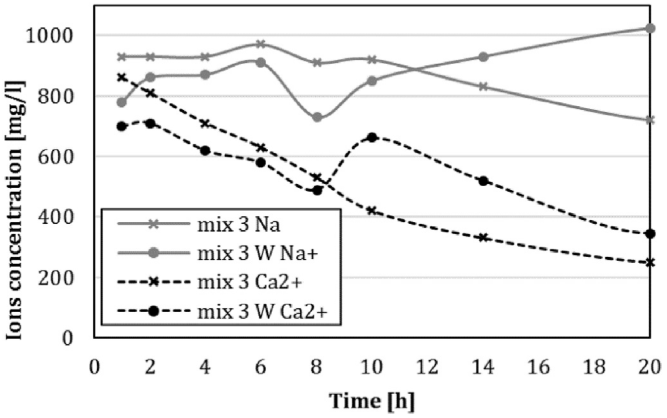
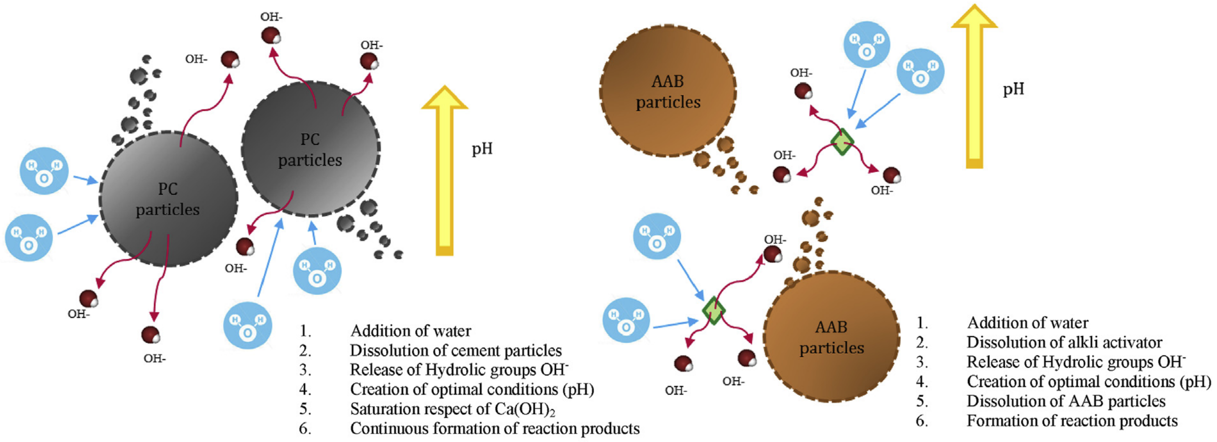


Fig. 5. Ionic behaviour of the Mix 3 and Mix 3 containing wood (Mix 3 W).

Based on the results of Mix 1 and Mix 2, a hybrid binder consisting of AAB and Portland cement (Binder 3) is studied to investigate the effect of cement on providing additional Ca^{2+} and OH^- ions, which leads to a more stable and prolonged reaction. The ionic behaviour of Ca^{2+} and Na^+ in Binder 3 is presented in Fig. 5. When wood is present, the Ca^{2+} ion concentration is lower compared to the reference until 8 h due to the sorption of the wood, while it follows a similar trend as the reference, indicating that reaction products are formed by the consumption of ions. Afterwards the Ca^{2+} concentration starts to fluctuate by the dissolution of cement,



(a) (b)

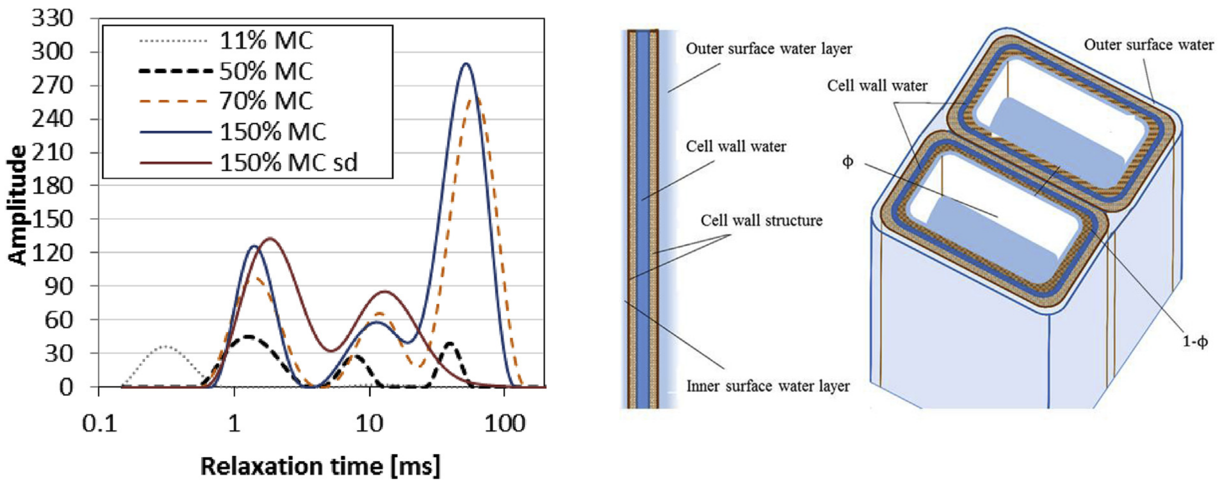
Fig. 6. Reaction mechanism of (a) OPC and (b) one part alkali-activated binder (AAB).

which provides Ca^{2+} that favours the formation of a C-A-S—H gel compared to N-A-S—H.

To summarize, it is clear that the ionic behaviour in the presence of wood strongly depends on the reaction mechanism of the used binders (Fig. 6) as mentioned in (Provis, 2014; Gao et al., 2015). Portland cement is able to react and stabilize the pH by providing OH^- and Ca^{2+} ions, leading to a continuous reaction, whereas the alkaline binder (Binder 2) rapidly loses OH^- ions, due to the interaction with wood. In order to reduce this influence, a replacement of the alkaline binder by 30% cement (Binder 3), acting as a buffer to provide OH^- and Ca^{2+} ions, enables the further reaction.

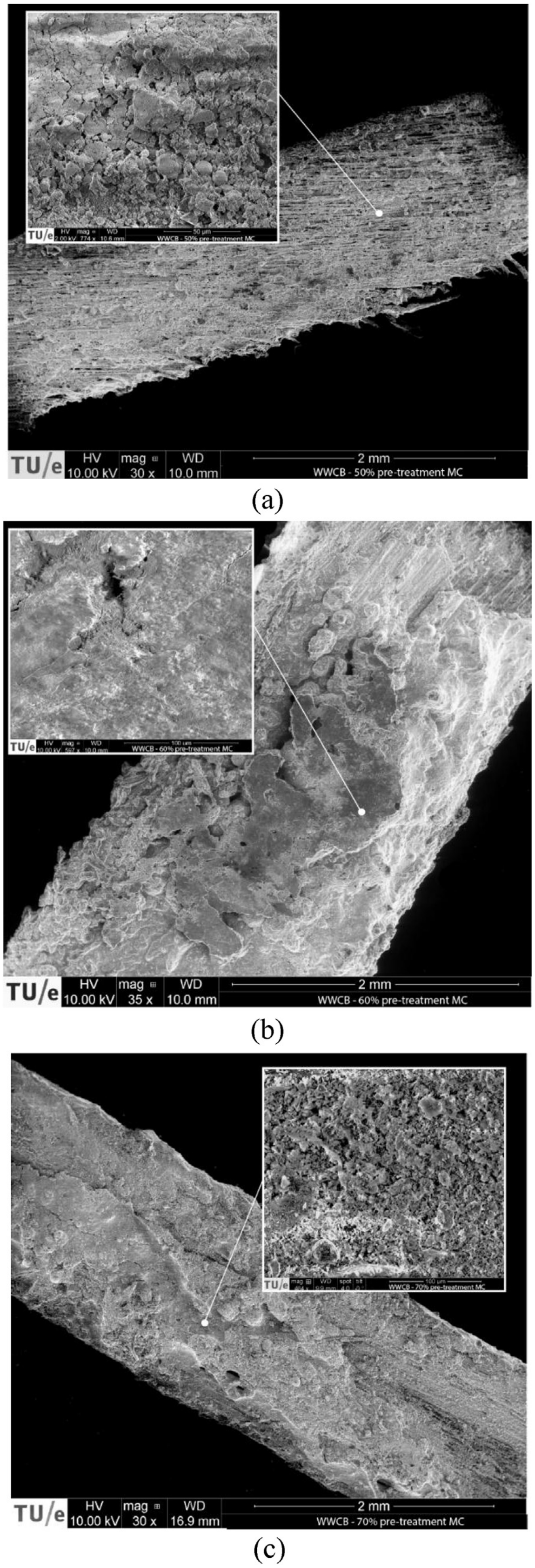
3.5. *Position of the absorbed water in wood wool strands*

Fig. 7a presents the proton NMR spin-spin relaxation time (T_2) spectra of the investigated wood wool strands. Different moisture contents were applied in order to identify the bonding trends and location of liquid water when pre-treating the wood as visualised in Fig. 8b. Wood strands with a moisture content (Mc) of 11% (by dry mass of wood) shows only one peak at a relaxation time T_2 less than 1 ms, which is assigned to hydrogen bonded water in the cell walls. When increasing the moisture content to 50% and then to 70%, a second and third peaks become noticeable. The first peak shifts to the right, leading to a higher relaxation time of >1 ms (Felby et al., 2008). The second peak, related to the water in the lumen by capillary forces, remains at around 10 ms (Araujo et al., 1993; Zhang et al., 2014). This relaxation time corresponds to spruce wood and can differ between different species (Araujo et al., 1992; Fourmentin et al., 2016). The third peak, with a relaxation time of 50 ms, indicates the position of surface water. The total peak height and the area beneath the curve are increased for Mc 70% compared to Mc 50%, showing a higher amount of water present as the peak as well as the area are considered as proportional to the amount of water within a characteristic pore range (Fourmentin et al., 2016). The peak is further increased when increasing the water content to



(a) (b)

Fig. 7. (a) T_2 relaxation times of wood wool with a Mc of 11, 50, 70, 150% and a surface dried wood wool with a Mc of 150% (150% Mc sd). (b) Visualisation of the position of water, where Φ represents the voids. In case of fully saturated wood (green wood), all the void spaces are filled. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



(a)

(b)

(c)

Fig. 8. SEM pictures of boards made with Binder 3 using 2.0 mm width strands (a) 50%, (b) 60% and (c) 70% pre-treatment moisture content.

150%. While removing the surface water results in the disappearance of the third peak (see sample 150 Mc sd in Fig. 7a), which confirms that the third peak positioned at 50 ms is attributed to the surface water.

From the results it is evident that when the wood wool has a Mc of 50%, a water layer on the surface starts to form and a further increase of the moisture level would increase the water layer thickness found on external surfaces (Hunger and Brouwers, 2009; Yu and Brouwers, 2011). Therefore, it needs to be evaluated if applying a Mc of 50% the absorption of liquid in the cell walls and lumen is sufficiently reduced to ensure the binder react properly.

3.6. *Evaluation of pre-treatment*

The alkali pre-treatment was designed based on the pH reduction presented in Fig. 2 of Section 3.2. For the one part AAB (Binder 2), a NaOH concentration of 8.5% based on dry wood was added to the system (starting pH 13) and for alkali activated slag (Binder 4) 28.5% (starting pH 13.5), both with a Mc of 60%. The solution was then sprinkled on the wood wool prior to the addition of the binder.

The flexural strength of all samples are listed in Table 6. It is noted that lignocellulosic materials often cause significant standard deviation, which is hence not considered in the present study. The samples using Binder 1 (B1), Binder 2 (B2) and Binder 4 (B4) resulted in a 10-day flexural strength of 1.9, 1.8 and 2.3 MPa and an apparent density of 399, 388 and 420 kg/m^3, respectively. This confirms the validity of the alkali-pre-treatment, as without pre-treatment the composites could not properly harden and no strength is developed in the produced composites. Regarding the water pre-treatment applying a hybrid binder, for Binder 3 (B3) and Binder 5 (B5) a 10-day flexural strength of 1.6 and 2.0 MPa with an apparent density of 357 and 430 kg/m^3 are found, respectively, showing a proper hardening is achieved when applying hybrid binders. Table 6 illustrates the flexural strength of composites using Binder 3 after applying different amounts of water treatment (Mixes B6-B8). Although the influence of density cannot be ignored, an optimum flexural strength is reached for Mix B8 applying a Mc of 60% (Fig. 8b). It is revealed by SEM that a proper reaction did not occur when applying a Mc of 50% (Fig. 8a), while a high Mc value of 70% indeed results in an increase of the porosity by the diluting effect (Fig. 8c), which negatively influences the strength. In the design of the pre-treatment for composites, the Mc of 50% was found to be not optimal since it did not take into account the distribution of the alkali activator and binder on the wood wool surface, and, a 10% increase of Mc is found to be effective for optimal composite properties.

3.7. *Environmental impact*

In the present study, the environmental impact is evaluated by only assessing the CO_2 footprint of the used materials. Although a complete cradle to grave life cycle analysis can provide a more comprehensive picture, the environmental impact analysis based on materials can also deliver a profound indication. This because the production process is kept similar. The transport distance in the Netherlands, is comparable to the initial used binder, with the AAB having the advantage of a lower density, hence, CO_2 footprint for transport. For Binder 2 (one part AAB), the low CO_2 footprint of the binder positively reduces the CO_2 footprint by 72.9% (Table 7) despite the NaOH pre-treatment. For Binder 3, no alkali pre-treatment is required but the use of 30% cement leads to a slight increment of the CO_2 footprint compared to Binder 2, but is still 61.5% lower compared to Binder 1. Application of GGBFS with an alkali activator and an alkali pre-treatment (Binder 4) leads currently to an increase of the CO_2 footprint compared to Binder 1

Table 7
Environmental consideration.

Binder No.	Pre-treatment	total CO_2 eq. per kg of mixture	total CO_2 eq. per kg of treatment	CO_2 footprint composite%
1	Water	0.150	–	Ref
2	NaOH	0.018	0.022	−72.9
3	Water	0.058	–	−61.5
4	NaOH	0.099	0.075	+16.0
5	Water	0.115	–	−23.8

(Portland cement) by 16.0%, which is attributed to the significant amount of NaOH used to pre-treat the wood wool (See Table 7). Adjustment of the pre-treating method to lower the environmental footprint for this mixture by exploring other sources of OH^-, or reducing the amount of alkali in the pre-treatment will be subject for further research. It is indicated that an alkali activated binder with a higher initial pH requires a larger amount of alkali for wood pre-treatment. Instead Binder 5, the hybrid binder containing alkali activated slag and cement (Binder 4 and Binder 1) requires no pre-treatment, achieving a 23.8% reduction of the CO_2 footprint hence, a proper pre-treatment is essential in successfully applying the alkali activated binder in such lignocellulose based environment.

4. Conclusions

This study addresses the interaction between alkali activated binders and lignocellulose wood wool strands. The behaviour of lignocellulose under different alkaline environments and the effect of lignocellulose on the ionic behaviour of Ca^{2+} and Na^+ in different binders are studied. The microstructure, treatment of wood wool and position of absorbed liquid in wood wool are evaluated. The present findings lead to a successful and industrially applicable design of a sustainable wood composite with comparable properties as references but with a significantly lower environmental footprint. Based on the obtained results, the following conclusions are attained:

- Wood wool is able to neutralize 53% of the initial OH^- ions, leading to a reduction of the pH from ~13 to ~12.6 in 4 h. As a result, the reactivity of alkali activated binder is negatively affected and reaction products are altered.
- The ionic uptake of wood results in insufficient reaction of the alkali-activated binder that can be compensated by (1) additional OH^- from an alkali pre-treatment or (2) substitution of the alkali activated binder by 30% cement.
- Depending on the required starting pH of the used Alkali activated binders, a OH^- content of 8.5% (Binder 2) and 28.5% (Binder 4) on dry mass of wood needs to be applied to ensure sufficient ions are present in the early reaction stage.
- The NMR results indicate that an addition of 60% water on dry mass of wood is most suitable to pre-treat the wood wool, resulting in the highest mechanical properties attributed to the less porous reaction products.
- Application of 100% alkali-activated binder with proper initial pH (Binder 2) or a hybrid binder (Binder 3) demonstrate very promising results, especially indicated by a remarkable CO_2 footprint reduction by 72.9 and 61.5% compared to a pure cement system (Binder 1).

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2018.09.220.

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