Development of sustainable and functionalized inorganic binder-biofiber composites

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This thesis addresses the performance-based design and evaluation of lignocellulosic cement composite boards, which are commercially known as wood wool cement boards (WWCB). The origin of WWCB goes back to around 1920 and is still popular nowadays.

This thesis starts with an introduction of WWCB by explaining its ingredients and the production process. Next, the retardation of sugars on cements is evaluated, providing new insights into the retardation mechanism when combining wood and cement. To reduce the environmental footprint of the boards, implementation of supplementary materials and the use of alkali-activated binders are studied. An orientated study is then performed on increasing the functionality of the boards by making it air purifying using the fundamental insights in the surface morphology. Since one of the main WWCB properties is sound absorption, a study is performed to characterize and to predict the sound absorption of WWCB by using impedance models. Finally, the disposal of commercial WWCB after its service life time is considered, leading to waste wood incineration and contamination of residues that require the design of economical feasible treatments.

Development of sustainable and functionalized inorganic binder-biofiber composites

Guillaume Doudart de la Grée
Development of sustainable and functionalized inorganic binder-biofiber composites

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Development of sustainable and functionalized inorganic binder-biofiber composites

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof.dr.ir. F.P.T. Baaijens, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op maandag 17 September 2018 om 11.00 uur

door

Guillaume Claude Hendrikus Doudart de la Grée

geboren te Helmond
Dit proefschrift is goedgekeurd door de promotor:
prof.dr.ir. H.J.H. Brouwers
Dedicated to my brother Jeremy Doudart de la Grée
(April 26, 1977 – June 17, 1997)
Preface

My PhD journey started on the first of October 2012. At that time my main goal was to broaden my knowledge in building materials and implement the gained knowledge in development of improved wood cement composites. Interestingly, performing research to fulfill my goals was only a part of the journey and my PhD involved much more than I ever could have imagined. Presenting science, writing articles, working in an innovative environment, traveling internationally and meeting people with cultures from all around the world made this period of my life very special. Therefore, this section is dedicated to all the people that shared this ‘journey’ with me providing support and help in many different ways.

First, I would like to express my gratitude to my promoter prof.dr.ir. Jos Brouwers who gave me the opportunity to join his research group and patiently supported and encouraged me in many phases of my PhD. Jos, thank you really very much, you inspired me a lot in both research and professionalism and I’m grateful that we got to know each other so well. Next, I would like to thank my daily supervisor dr. Qingliang Yu, for the many guidance he provided which goes beyond research. I learned a lot from you until this very moment and it was a true honor to work with you on this challenging journey.

I also appreciate the financial support from STW (Project 11861) and of the sponsor group who funded this research. Special thanks are given to: dr. Jan van Dam (Wageningen UR) for all his kind support on the lignocellulose based knowledge during this study; dr.ir. Arno Keulen (van Gansewinkel Minerals) for the knowledge and practical issues on working with industrial byproducts; Mr. Jan Mencnarowski and Mr. John van Eijk (Knauf Insulation) for the valuable insights regarding the industrial production of WWCB. Mr. Paul van Elten (Eltomation) for the valuable knowledge of the WWCB history and production plants for producing WWCB. Ing. Peter de Vries (ENCI) for the support and guidance related to implementation of Portland Cement and overcoming retardation issues.

I am grateful to all the members of my core committee, prof. dr. ing. Sofiane Amziane, prof. dr. ir. Nele De Belie, dr. Jan van Dam, dr. ir. Maarten Hornikx, prof. dr. ir. Jos Lichtenberg for their constructive comments on my manuscript and for agreeing to be members of my PhD defence committee.

During my stay at the TU/e I have met some wonderful collages and I would like to address my appreciation to some former and current colleagues for their help and support: A. de Korte, M. Florea, P. Spiesz, A. Lázaro, G. Quercia, A. Taher, S. Lorencik, R. Yu, P. Tang, C. Straub, P. van der Wouw, X. Gao, B. Yuan, K. Schollbach, K. Kochová, Q. Alam, P. Li, Z. Qu, V. Caprai, E. Loginova, G. Gauvin, A. Kaja, H. Karimi and G. Liu.

My appreciations are also expressed to Gertjan Maas, Peter Cappon, Anneke Delsing, Harrie Smulders and Jan Diepens for their help in the laboratory. My appreciations are also expressed to our lovely secretaries of the unit BPS.

At the TU/e I had the chance to not only work on my own PhD project but also to work on a granted idea ‘the leafroof’ and on providing several master courses. During this process I had the chance to work with Bert van Schaik, Henk Schellen, Alexander
Rosemann and Mark Cox who provided valuable feedback and knowledge and helped me with my professional carrier.

During my PhD I had the chance and honor of supervising two special master students: Veronica Caprai and Bram Botterman with whom I shared the passion of working with wood cement composites and who contributed to this thesis, opening new perspectives. Furthermore, I would like to express my gratitude to the master students Marco de Groot, Jonathan Ezechiëls and Thijs van Druenen. Thank you for your help in assisting my research and hopefully my supervision has been helpful for your professional careers.

Finally, I need to express my appreciations to my supporting family. Mum and Dad, thank you for always being there for me and trying to understand what I was actually doing at the TU/e. My thanks are also given to my brother and sister for taking care of my son Nathan during the last years of my PhD. Finally, and most importantly, I want to express my appreciations and feelings to my wife, Adelya. We started together our PhD journey on the same date but in different BPS chairs. It was always nice having you near me and share our working experience. That we got married and got Nathan in this period was a blessing and a welcome change in life. There are not enough words that can express my feelings but know that I love you forever.

Guillaume Doudart de la Grée

Eindhoven, September 2018
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Chapter 1

Introduction

1.1 Background
Annually 16 million m$^2$ of wood wool composite boards (WWCB) are produced in Europe. The product is known since 1900, created from spruce or popular wood wool, using magnesium as a binder (Wolfe, 1999; Aro, 2004). In around 1920, after the invention of Portland Cement (PC) in the 19th century, cement replaced the magnesium as a binder leading to the creation of the nowadays known WWCB (van Elten, 2006). Because of the used cement, the term WWCB nowadays is also translated as wood wool cement boards. The boards became increasingly popular because of their high thermal insulating and sound absorbing properties gained by its high porosity and low density. In accordance with European Norm EN 13168 (formerly DIN 1101) the density of WWCB can range from approximately 360 up to 570 kg/m$^3$, although higher and lower densities are also possible. Consequently, because of the mineralization of the wood wool strands, the boards possess high resistance to bio-degradation (Pereira et al., 2006) and fire (Aro, 2004). Hence, the boards are applied in both buildings and constructions as roof and ceiling material, or as an exterior wall where a high durability and low maintenance is required. An illustration of WWCB is presented in Figure 1.1. The common raw materials of WWCB are wood wool strands (lignocellulose), cement and water (with sometimes the addition of dissolved salts). In the northern hemisphere mainly pine and spruce is used, in some countries also eucalyptus. The wood is shredded to long strands (length $\pm 250$ mm, width $\pm 1-3$ mm, thickness $\pm 0.05$ mm) and is dipped in a water-sodium silicate solution to accelerate the cement hydration. The wetted wood, together with cement (usually PC), is mixed and then spread on plywood moulds and pressed. Depending on the used distance holders, a composite of 15-50 mm thickness is obtained. After sufficient initial curing, e.g. after 24 hours, the product is removed from the mould and is left to cure further.

![Figure 1.1: Illustration of a wood wool cement board with a thickness of 15 mm.](image)

WWCB are falling under the category wood cement composite (WCC) and, compared to WCC, literature regarding the product is scarce. Therefore, information can only be
derived from manufacturers or the search for information needs to be diverted to the
general term WCC. WCC can be found under plenty of names depending on the wood
dimensions (see an overview in Figure 1.2) referred to as “wood-strand cement board”
(Aro, 2004), cement-bonded-wood particle board (Soroushian et al., 2003), cement-
bonded composite boards (Aggarwal et al., 2008; Ashori et al., 2011). The disadvantage
of using literature regarding WCC is the minor similarities with WWCB since the boards
are produced in different ways, under different conditions, using different lignocellulose
materials and face different challenges, hence, are in most cases less applicable for
WWCB. For instance, most WCC consist of micro and macro wood particles with a
reported inhibitory effect on the used binder resulting in lower mechanical properties.
Moreover, the use of smaller particles also requires a higher amount of binder, that
increases the density of the boards. Therefore, the mechanical, thermal and acoustical
properties significantly differ from the low density WWCB which are covered by a very
thin layer of binder having a solid content by volume of < 30%.

Figure 1.2: Visualization of wood types. From left to right with reduced dimensions: logs, lumber, veneer,
wood chips, wood strands, wood granules, wood slivers, wood shavings, wood flakes, wood wool, wood
fiber, wood dust, paper fiber, wood flour, and cellulose.

1.2 Raw materials

1.2.1 Cement

The use of Ordinary Portland Cement (PC) within WWCB provides many advantages,
like high mechanical strength and long service life. This property is due to a densification
of the matrix around the wood wool strands, known as “mineralization” (Semple and
Evans, 2004) occurring during the aging of the boards in an external environment. The
further formation of hydration products within the core of the cellulose fibers, and
perhaps also in the fiber cell wall, leads to an increment of strength and stiffness of the
panel (Bentur, 1989). Besides this, the mineralization allows outdoor applications where
the weathering of the boards only causes small dimensional changes (Simatupang and
Meanwhile, the manufacture of WWCB also involves some negative aspects as the PC production generates around 1 ton of CO₂ for each ton of cement (Provis and Bernal, 2014). During transport and production also fossil fuels are consumed and nitrogen oxides (NOₓ) and sulfur oxides (SOₓ) emissions are emitted, contributing to the greenhouse effect (Graham, 2003). Moreover, for many years, the economy operated as an open system, where raw materials were continuously consumed, returning in unused by-products in form of waste. To control the waste stream, effort is required in recycling and re-using of waste and only then accumulation of the environmental impact will start to reduce (Ehrenfeld and Gertler, 1997). Therefore, in recent years, many studies have been focusing on reusing and treating waste products (now seen as by-products) to be applied in existing and new materials (Wolfe, 1999; García et al., 2008; Cheah and Ramli, 2011; Ashori et al., 2012; Nazari et al., 2014; Tang et al., 2015; Wong et al., 2015).

Besides the environmental issues, the compatibility between cement and wood is still a studied matter. Soluble extractives of the wood wool strands could retard, even terminate, the hardening process of the cement. This phenomenon could be easily observed by monitoring the heat release over time during the exothermic hydration of the cement. Simatupang (1992) shows that the absence of peaks corresponding to the consumption of specific phase in the cement (C₃S and C₃A) or their shift is an evidence of this phenomenon. This inhibitory effect of wood on cement is mainly due to substances such as hemicelluloses, starches, sugars, contained in the wood fibers, which dissolve in the high alkaline environment (Fan et al., 2012). Therefore, the wood is stored and treated by e.g. soaking of the wood, treatment with Ca(OH)₂ and acceleration of the hydration of cement by additives like alkalis (Hachmi et al., 1990; Simatupang and Geimer, 1990; Jorge et al., 2004; Pereira et al., 2006; Fan et al., 2012) and chlorides or even pre-hydrated C₃S (Young, 1972) e.g. from the recycled concrete fines (Florea et al., 2014). However, some of these solutions are not always applicable, e.g. to materials like WWCB the use of chlorides is restricted by the EN 13168 to a very low quantity (≤ 0.06% in case of Cl3 level). This is because often the boards are assembled near reinforced concrete structures in which penetration of chlorides can cause erosion of the reinforcement and damage the structure (Lee and Short, 1989; Mencnarowski, 2014).

Ordinary Portland Cement is the second most-used commodities worldwide after water (Brouwers, 2010). Due to the high environmental impact many studies are performed on this topic. Among them, Damtoft et al., (2008) defines an optimization of the PC manufacture for the minimization of its CO₂ footprint. The application of bio fuel and alternative raw materials for the production of the binder such as limestone powder (LP), ground granulated blast furnace slag (GGBFS) and fly ash (FA) can lead to a maximum reduction in the CO₂ emission of 17% (Damtoft et al., 2008). Despite of those achievements, the PC carbon footprint needs to be further reduced. Among the potential alternatives, alkali activated binders (AAB) are very promising and can lead in case of concrete to a much lower environmental impact compared to the use of Ordinary Portland Cement.

The main difference between AAB and cement production is the avoidance of a high temperature calcination step, during the synthesis of FA or GGBFS. Although the minimal environmental impact of the production of those prime materials (Provis, 2014),
the use of hydroxide or silicate activation does increase the greenhouse effect (Duxson et al., 2007). Based on the carbon dioxide equivalence (CO₂-e), an evaluation of the CO₂ footprint of PC and some alkali activators can be done. CO₂-e is a term for describing different greenhouse gasses in a common unit. For any quantity and greenhouse gas type, CO₂-e signifies the amount of CO₂ that will have the same global warming potential (GWP) (Brander and Davis, 2012). Therefore, calculations of emitted CO₂-e (kg CO₂-e/kg material) is based on the sum of the contribution belonging to CO₂, CH₄, NO₂ and synthetic gasses emissions, developed during a specific activity and taking into account the embodied energy of the material. NaOH carbon footprint is mainly depending on its manufacture. It is produced with chlorine through the alkali process (processing alkalis with electrolysis). On the other hand, Na₂SiO₃ is produced by melting silica and sodium carbonate (Turner and Collins, 2013).

Table 1.1: CO₂ footprint of fly ash (FA), PC, NaOH and Na₂SiO₃ (Turner and Collins, 2013).

<table>
<thead>
<tr>
<th></th>
<th>FA</th>
<th>PC</th>
<th>NaOH</th>
<th>Na₂SiO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>kg CO₂-e/kg</td>
<td>0.03</td>
<td>0.82</td>
<td>1.92</td>
<td>1.51</td>
</tr>
</tbody>
</table>

The values in Table 1.1 take into account the CO₂-e for the materials manufacture. Although the alkali activators are characterized by high environmental impact, the quantity necessary for the activation of AAB will be much less compared to the use of PC. In case of AAB the real saving lies in the use of sustainable raw materials, as FA and GGBFS. The utilization of these prime materials will provide improvements connected to the removal of materials from landfill, and an alternative utilization of the waste streams (Duxson et al., 2007). Further developments of this technology can lead to the application of binding systems based on the partial or total replacement of PC, reducing to the minimum the PC content and also its environmental impact.

1.2.2 Wood

In Europe, mostly coniferous species (softwood), like spruce, are used to produce WWCB due to their high availability and lower degradation by the alkaline environment. This leads to a lower release of inhibitors compared to deciduous species (hardwood) (Beltran Sierra, 2011). Also the use of aspen, basswood, cottonwood, black willow and yellow-poplar is mentioned (U.S. Department of Agriculture, 1987). Lee and Short, (1989) concluded that WWCB can be produced by using hardwood species like southern pine and confirmed the use of cotton wood when pre-treating with 3% CaCl₂, 3% Na₂SiO₃ or plain water. Yellow polar could be applied when treated with CaCl₂ or Na₂SiO₃ and sweetgum when using CaCl₂. Some other suitable wood-species are presented in Table 1.2, making it clear that most wood species around the globe are feasible for production of WWCB, indicating that WWCB can be produced everywhere in the world (van Elten, 2015).

In this study, Spruce wood is mainly used and represents the largest part of the standing tree species in Sweden with approximately 44% and is one of the most commonly used wood species in the Northern Europe (Brändström, 2001a). Spruce consists of many
pores having a hexagonal shape as presented in Figure 1.3. Because of the high amount of voids, the wood wool strands have a porosity up to 63%. Due to this porosity, the thermal conductivity of oven dry spruce is 0.11 W/m·K (Simpson and Tenwolde, 1999; Niemz et al., 2010) that makes it suitable for lightweight thermal insulating panels. The thickness of the cell wall and amount of cell walls are determining the total porosity of the spruce wood and vary per season, e.g. in spring cell walls are thicker (2-3 µm) than cell walls in fall (+/- 7 µm) (Prošek et al., 2015). Furthermore, the cells are denser packed during fall compared to spring.

Table 1.2: Wood types successfully applied for WWCB production (van Elten, 2015).

<table>
<thead>
<tr>
<th>America</th>
<th>Australia</th>
<th>Europe</th>
<th>Africa</th>
<th>Asia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alophylilum</td>
<td>Acacia saligna</td>
<td>Abies pectinata</td>
<td>Aklonia boonei</td>
<td>Haktina</td>
</tr>
<tr>
<td>brasiliense</td>
<td>Casuarina spp</td>
<td>Abies Alba</td>
<td>Androstachys</td>
<td>Agathis dammara</td>
</tr>
<tr>
<td>Cedrela</td>
<td>Exocoecaria agallocha</td>
<td>Castanea sativa</td>
<td>Anigre</td>
<td>Altingia excelsa</td>
</tr>
<tr>
<td>Cedra pentandra</td>
<td>Picea Abies</td>
<td>Neoamarckia kaedamba</td>
<td>Artocarpus chaplasha</td>
<td></td>
</tr>
<tr>
<td>Pinus caribaea</td>
<td>Pinus Sylvestris</td>
<td>Brachystegia leonensis</td>
<td>Bombax ceiba</td>
<td></td>
</tr>
<tr>
<td>Picea Sitchensis</td>
<td>Picea Abies</td>
<td>Tiama Entandrophragma angolense</td>
<td>Toona ciliata</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.3: Scan of spruce wood wool strands (Doudart de la Grée et al., 2013).

Wood structure

The wood pores as visualized in Figure 1.4 showing the open parts of tracheids. Tracheids, which comprise over 90% of the total cell wall volume, serve as mechanical support as well as conduction of water (Brändström, 2001). The voids within a tracheid are called lumen. Tracheids consist of single elongated cells with lengths between 2-4 mm, a diameter of 20-40 µm, wall thicknesses of 2-10 µm and are arranged longitudinally (e.g. parallel to the growth of the trunk). The tracheid cell walls are constructed in a composite structure of a primary and a secondary wall. The primary wall and secondary wall consist mainly of cellulose and lignin (Gindl et al., 2004). The fibrils are composed by a practically equal amount of hemicellulose and polysaccharides. This lignin is an important factor in the determination of the strength of wood because it is binding the individual cells together (Gindl et al., 2004).
Studies have indicated a difference in lignin content between wood earlywood, harvested in an early stage of the year (e.g. start of growing season) and latewood, wood harvested in a later stage (e.g. second half of growing season) (Prošek et al., 2015). Considering this, the strength of wood is a result of the composite formed by the interaction between cellulose and lignin (approximately 25-33% of dry wood volume) wound around. In Table 2.2 of Chapter 2 the chemical composition of spruce wood is provided.

Moisture content

Tracheids enable the transport of water through the pores (Brändström, 2001). The presence of water in softwood can be explained by the lumen in the tracheids that serve as water transfer, establishing a dissemination of water through the whole trunk. One month after harvesting the water content can decrease to approximately 31% of its original value (Laurila and Lauhanen, 2010). The moisture content \( (Mc) \) of spruce can reach values up to 53% directly after trunk harvesting (Laurila and Lauhanen, 2010). \( Mc \) can be determined according to

\[
Mc = \frac{m_i - m_{cell}}{m_{cell}} \times 100
\]  

(1.1)

where \( Mc \) is the moisture content of wood in [%]; \( m_i \) is the mass of water impregnated wood in [g] and \( m_{cell} \) is the mass of wood after 24h oven drying in [g]. After oven drying, wood wool strands absorb moisture naturally from the environment although temperature and relative humidity depending as illustrated in Figure 1.5 using the Hailwood and Horrobin (1946) equation for wood.
As for the $Mc$, moisture can be located in the cell walls until 30% of its dry-oven mass (saturation point of wood) and subsequently in the volume of the lumen. When the cell walls are completely filled with water, the maximum expansion of the cell wall volume is reached. When observing wood, the total volume of wood can be expressed as the volume of the wood cell walls ($V_{cell}$) (expressed as a solid) and the volume of the voids of the wood ($V_{voids}$). The additional volume which is created by the expansion of the cell walls due to the absorbed moisture ($\Delta V_{void}$) together with the volume of the lumen ($V_{lumen}$) can be expressed as the total void volume of the wood ($V_{voids}$) as presented in Figure 1.6. The approach of having a fixed volume of wood but varying $V_{voids}$ differs from Siau (1984) who defines a total volume change, and by that a varying density of the cell wall with the $Mc$ of the wood. The derivation of the known equations following the fundamental consideration is described on the next pages.

Figure 1.5: Moisture content absorption based on relative humidity (Hailwood and Horrobin 1946).

Figure 1.6: (a) SEM picture of the cross section of a cement covered wood wool strand; (b) Enlargement of the cell walls and lumen, the cell wall structures are composed of an inner, middle and outer layer, a primary wall and middle lamella; (c) schematic representation of the total volume of wood that consists of $V_{voids}$ and $V_{cell}$ of which $V_{voids}$ is composed of $\Delta V_{void}$ and $V_{lumen}$.
Because the cell walls swell and shrink in the range of 0-30% $MC$, $V_{voids}$ increases or decreases, respectively but remains stable when the $MC$ is higher than 30% based on oven-dry mass. In case the $MC$ has reached the saturation point or higher, the volume of the cell walls stays constant and the volume of the wood is known as the green volume of wood.

Using the approach of having a fixed volume of wood the maximum $MC$ ($MC_{max}$) can be calculated when $V_{voids}$ is completely filled with water:

$$MC_{max} = \frac{\rho_w \times V_{voids}}{m_{cell}} \times 100$$  \hspace{1cm} (1.2)

In which $MC_{max}$ is the maximum $MC$ of the wood [%]; $\rho_w$ is the density of water in [g/cm$^3$] and $V_{voids}$ the void volume of the wood [cm$^3$]. Furthermore, a common expression used in the wood industry is the specific gravity of wood (determined by measuring the oven-dry mass of the wood divided by the green volume of the wood) divided by the specific density of water following:

$$G_b = \left( \frac{m_{cell}}{V_{cell} + V_{voids}} \right) / \rho_w$$  \hspace{1cm} (1.3)

In which $G_b$ is the dimensionless specific gravity of wood (measured by using the green volume of wood) [-] and $V_{cell}$ the volume of the cell walls [cm$^3$]. Eq. (1.3) can be rewritten as:

$$V_{voids} = \frac{m_{cell}}{G_b \times \rho_w} - V_{cell}$$  \hspace{1cm} (1.4)

Substituting eq. (1.4) into eq. (1.5) yields:

$$MC_{max} = \frac{\rho_w \times \left( \frac{m_{cell}}{G_b \times \rho_w} - V_{cell} \right)}{m_{cell}} \times 100$$  \hspace{1cm} (1.5)

$m_{cell}$ can be rewritten as:

$$m_{cell} = \rho_{cell} \times V_{cell}$$  \hspace{1cm} (1.6)

In which $\rho_{cell}$ is the specific density of the cell walls in g/cm$^3$.

Substituting eq. (1.5) and (1.6) into (1.7) yields:

$$MC_{max} = \frac{\rho_w \times \left( \frac{\rho_{cell} \times V_{cell}}{G_b \times \rho_w} - V_{cell} \right)}{\rho_{cell} \times V_{cell}} \times 100$$  \hspace{1cm} (1.7)
Substituting the value of $\rho_{\text{water}}$ (1 g/cm$^3$), Eq. (6) can be rewritten as eq. (1.8) by:

$$M_{c\ max} = \frac{(\rho_{\text{cell}} - G_{b})}{\rho_{\text{cell}} \times G_{b}} \times 100$$  (1.8)

According to the U.S. Department of Agriculture (1987) the dimensionless specific gravity of spruce wood, $G_{b}$ is 0.36. Based on the specific density of cell walls $\rho_{\text{cell}}$ is 1.54 g/cm$^3$, $M_{c\ max}$ according to eq. (1.8) is 212%. Practically such high $M_{c}$ does not easily occur, since wood logs will not be fully saturated with water. However, in case of wood wool strands, this condition occurs easier due to the small dimensions of the wood wool strands. The ability of wood to absorb high amounts of water, makes the production more challenging since different cement types require certain water amounts to react and in the above mentioned production process sprinkling wood wool with cement requires cement to take water from the wood wool. Insufficient water will therefore result in insufficient hardening of the cement while in case excessive moisture is present in the lumen of the wood wool strands, this moisture will be liberated during the press curing of the composite and cement paste migrates to the bottom of the boards.

1.3 Production process WWCB in the Netherlands

Since the method of manufacturing a material influences the final properties of the produced materials, the production process needs to be well understood to ensure low deviations in the product’s performance. The first impression that people have when introducing WWCB is that it is a low tech material. In reality many factors are at hand which gives the material its unique features. In the following sections, different facets of the production processes to produce WWCB are described. In short, the process is divided into four main stages, i.e. conditioning of wood logs, shredding of wood logs, forming of the composites and curing of the composites. The influences of several parameters on the above stated stages of the production process are afterwards briefly discussed and analyzed in relation to the most important properties of the boards. Based on the obtained findings, suggestions for improvements are provided. Figure 1.7 shows a visualization of a wood-log, wood wool strands and a WWCB.

![Visualization of wood-log, wood wool strands and WWCB](image)

Figure 1.7: Visualization of the (a) Wood logs; (b) Wood wool strands; (c) WWCB. Pictures made by Botterman(2016).

Forest trees, preferably PEFC or FSC certified, such as pine, spruce, poplar or eucalyptus (van Elten, 2006), are harvested at 30-50 cm above the ground level, whereas multiples of 0.5 m are used for the production of WWCB. The diameter of the logs should satisfy the required diameter range of 16-26 cm. The branches and bark of the trees are removed on site. After sawing, the wood logs, known as green wood, are stored on site for 3-6
months in order to leach the soluble sugars out and reduce the moisture content \((Mc)\), also known as wood seasoning. The wood logs and wood wool strands further described in this study are all from Norwegian spruce (or simply termed spruce wood). Initially the \(Mc\) depends on the age of the wood log, type of wood, seasoning of the wood log, geographic origin etc. The measurements of 8 green and 8 seasoned spruce wood logs in February 2015, based on mass of oven-dry wood indicate a \(Mc\) of 63-102% and 22-63%, respectively. The chemical analysis of green and seasoned spruce wood showed only minor differences and are likely caused by its natural deviation rather than the influence of seasoning. The production process of WWCB starting from the seasoning of wood logs follows the procedure, as presented in Figure 1.8.

First, the outdoor stored wood logs are cut into blocks of 50 cm in length, screened for metal parts and cut into 25 cm pieces and shredded to wood wool strands. Although there are still machines that produce longer strands, the length of the wood wool strands is reduced by the introduction of the Eltomatic Rotating Wood Wool Machine also named CVS-16 in which CVS stands for continuously variable speed and 16 the amount of slot knives (van Elten, 2015). The final dimensions of the wood wool strands are 25 cm in length, 1-3 mm in width and 0.15-0.4 mm in thickness. The \(Mc\) of the produced spruce wood wool strands varies between 13-27% (determined on 17 randomly taken samples during the production of wood wool strands in June and July 2014, at Knauf insulation). The \(Mc\) of the wood wool strands is always lower than the initial \(Mc\) of the outside stored wood logs that enter the cutting machine because part of the moisture is evaporated during the shredding process in which fast rotating (high temperature) knives are used. The variation of the \(Mc\) within the wood wool strands can be attributed to the nature of the wood, as indicated before, but also to the storage conditions exposing the wood logs to outdoor climate conditions as presented in Figure 1.9. During dry days water evaporates while after rainy days, the measured \(Mc\) in the wood wool strands is increased. Still on average \((Mc \sim 18\%)\) the moisture content is lower in June and July.
(summer period) compared to the earlier reported moisture content in February (winter period).

![Figure 1.9: Weather conditions in June and July (data from weather station Oosterhout the Netherlands) and Mc of the wood wool strands (based on oven-dry mass). The bars indicate rain periods.](image)

After shredding, the wood wool strands are dipped in a water bath to increase the $Mc$, which is later needed for the cement hydration. Due to the high water uptake of the wood wool strands the wood wool strands are pressed with a roll press to decrease the water content. The opening of the press is adjustable depending on the water content of the wood wool strands.

The most influential factors regarding the water uptake are the initial $Mc$ of the wood wool strands, the dimensions of the wood wool strands (surface area), the density of the wood wool strands (cell walls that chemically can bond water and pores that can capillary absorb water) and the opening of the roll press (Figure 1.10a). Moreover, $Na_2SiO_3$ (sodium silicate) can be added into the water bath to enhance the cement reaction by the availability of dissolved Si ions which react with the Ca ions from the cement to produce C-S-H gel and elaborated heat. Afterwards, the wet wood wool strands, together with cement powder, are fed into a rotating mixer. The amount of cement is depending on (1) the amount of wet-wood wool; (2) the mass of the wet wood wool strands on the belt and (3) the mass variations of the belt (Figure 1.10b).

The mixing time is related to the amount of wet-wood wool that is fed to the mixer and the amount of cement covering the wood wool strands. The irregular flow of wet wood wool strands is continuously controlled by an electronic device. The double distribution machines spread two different layers of a continuous mat of wood wool strands cement
on top of each other into the molds. Based on the type of WWCB, e.g. made of 1.0, 1.5, 2.0 or even 3.0 mm wide wood wool strands with various board thicknesses, the distribution machine allows higher or lower quantities of mineralized wood wool strands, controlled by the program.

![Image](a)  
**Figure 1.10:** (a) Pressing belt to reduce moisture content of the wood wool strands after soaking in a water bath; (b) Weight measurements of wet wood wool strands and belt.

After having passed a hydraulic pre-press roll (small force, enough to press the composite together), the molds are separated by a circular saw and moved to the hydraulic stacking press. This machine stacks the molds with fresh material (the mold height is used as a reference for the board thickness). When the maximum stack height is reached, the stack is moved out and stored under pressure again for 24 h (e.g. by a concrete block of 1500 kg). After the setting of cement, the boards are taken from the molds for further curing, while the molds can be cleaned and oiled for re-use.

After a storage period of 10 days, the boards are transferred into an oven at 130-160 °C for at least 30 min to remove the excess water, to limit the shrinkage of the boards and to reduce the unit weight. The Mc of the boards after heating is around 12% by dry mass of WWCB. Finally, the boards are painted, stacked and packed.

### 1.3 Influential parameters and consequences

*Shredding the wood wool strands (geometry)*

The wood logs (25 cm in length) are shaved in the CVS-16 by being pressed against the knives which are placed in a rotating disk (Figure 1.11a), and by this an external load is created on both the knives and wood logs. This load would be higher when applying long wood logs, hence, the length is restricted. Depending on the aesthetic and functional requirements of the boards, wood wool strands with different dimensions can be produced with a width of 1-3 mm and a thickness of 0.15-0.5 mm. The width depends on the distance of the grooves of the knives (van Elten, 2010) (Figure 1.11b). The thickness of the wood wool strands depends on four different factors: (1) the speed ratio between the rotating knives and the feeding speed of the wood logs; (2) the wearing/abrasion of the knives, e.g. after a certain production time the knives need to be replaced since the thickness of the strands decreases; (3) the force used to press the wood logs against the
knives; (4) the Mc and density of the wood logs. Regarding the latter, fresh logs contain high amounts of moisture, and when the content is too high (> 35% based on dry mass), short and thin wood wool strands are produced with a thickness of ± 0.240 mm compared to ± 0.340 mm when using “dry” wood-logs (Mc < 30%). This is caused by the increased resistance of the wood-logs against compression when the pores in the wood wool strands are filled with liquid water, hence, the knives will penetrate less deep into the wood-log and no proper wood wool strands are produced (van Elten, 2015). In the case of logs with a high Mc, the feed speed through the knives can be increased (up to a certain level) to create thicker wood wool strands. However, this results in a higher load on the knives that leads to a reduced life time and increased energy consumption of the machine. Furthermore, the wet wood wool strands clump easily together with the dust and eventually lead to the obstruction of the output passage of the machine. In overall, the thickness of the wood strands are difficult to control, and highly depend on the used machine settings and the used wood logs. In case of wood logs with a low Mc (< 20%), there will be more friction (measured energy consumption is 10% higher compared to wood logs with a Mc of ± 30%) that leads to an increased temperature of the knives and local combustion of the wood wool strands. Therefore, it is recommended to keep the Mc between 20-35% on dry mass of the wood, meaning that the cell walls of the wood are almost or completely saturated but the location of liquid in the lumen of the wood is limited. In this way the friction between the wood logs and the knives is reduced leading to a lower energy consumption of the knives and prolonged lifetime (Figure 1.11c).

**Figure 1.11:** (a) Rotating disk with 16 knife slots; (b) Example of a knife; (c) Schematic overview of the energy consumption of the knives during the production process for a fluctuating and stable log input.

Figure 1.12 presents the apparent density of 370 wood logs. The observed density varies between 400 and 700 kg/m³, fluctuating moisture contents and the density of the log (amount of cell wall structures present in the wood). When monitoring the energy consumption in time to shredder the wood logs, the energy consumption varied between 35-54% in which 100% equals 160 kW with 900 rpm. Therefore, a test is performed where the wood-logs were separated into three different density classes of which the highest density class between 580-680 kg/m³ is shredded and presented in Figure 1.13. It is found that the energy consumption by shredding this high density class fluctuates around 51% with a deviation of 1%. Based on the energy consumption of the high density class it is recommended to separate them in density classes and store the wood logs with higher density classes longer to reduce the moisture content. In this way the energy consumption can be reduced and the life time of the knives can be prolonged. Another method would be kiln seasoning the wood logs. Although this requires a heat source.
Soaking of the wood

Because during the industrial production of WWCB the amount of cement applied is depending on the wet wood wool entering the mixer, the moisture content of the wood wool can have significant impact on the final composition of the board e.g. wood, water and cement amount. For example, in the first case there is a board produced with 1 m$^3$ of wood wool strand having a $M_c$ of 230%, and 1100 kg of binder. In the second case there is a wood wool strand volume of 1.2 m$^3$ used with a lower water content e.g. 190% and again 1100 kg of binder. The properties of both boards will be different. This since in case two the same binder amount need to cover more wood wool surface. Moreover, the hardening of the board will be negatively influenced due to the lower amount of moisture available for the cement hydration.
The moisture content of the wood wool strands is depending on soaking of the wood wool strands in a water bath and subsequently removing of the water by pressing in a role press. The fluctuating amount of wood wool strands through the roll press (the wood wool is not homogenously distributed over the belt) leads to a fluctuating distance between the cylinders of the role press, hence, the amount of water within the wood wool strands is deviating. The measurements of 17 randomly taken samples of wood wool strands after the water bath and role press indicate a $M_c$ varying between 182% and 295% (Mencnarowski, 2014).

Therefore, a study is performed to investigate the possibility of characterizing the influence of moisture on the total wood amount by reproducing several board compositions of already produced boards that are cured for 10 days. The moisture amount is measured by drying the boards in an oven at 100 degrees for 24 hours and calculate the mass loss. The wood amount is determined by measuring the loss on ignition at 750 degrees for 1 h (Quiroga and Rintoul, 2015). The remaining mass amount is accounted as unreacted binder. Note that the values are only used for indicative purposes, this since there is a small percentage of unburned wood wool particles, which are accounted as binder. Moreover, there is an amount of chemical bound water that is released by dehydration of the binder and is accounted to the wood. To define the latter is found to be difficult since the hydration degree of the binder is varying because of the moisture uptake of the wood wool. The results of the study in which the binder amount is linked to the total wood wool and moisture amount is presented in Figure 1.14a revealing a clear relation which is a result of the designed input recipe (the fixed wood + moisture to binder ratio), which controls the dosing unit of the binder. In this case the moisture amount presents the water contained by wood (measured by oven drying) plus added water for cement hydration. In Figure 1.14b the obtained wood amount and moisture amount are presented. It demonstrates there is no clear relation between the moisture amount and wood amount, which is caused by a number of factors including the wood density, moisture uptake, and the capillary water present in the voids of the hardened binder.

Nevertheless, in this production process, ideally, the wood wool strands should first be acclimatized to reach for instance the fiber saturation point to obtain a constant mass. An additional amount of water can then be added, taking into account the water amount required for the binder to hydrate, and the amount of water that the wood wool strands will keep due to chemical and capillary forces.
1.4 The influence of moisture and binder amount

In addition to the previous studies, a study is performed on the bending and compressive strengths of boards produced with a higher (1.5 HB) and lower amount of binder (1.5 LB). The results of this study are presented in Figure 1.15. Due to confidential reasons, the amounts (recipes) are not displayed and the performed study is only indicative. Initially the aim of producing boards with a higher binder amount is to better cover the wood wool strands and by that to increase the fire resistant properties of the boards. Moreover, the hypotheses that boards made with more binder lead to higher mechanical properties can be answered. Figure 1.15 indicates that when observing the compressive and bending strength results it is difficult to distinguish between lower and higher binder amounts. This is proved to be caused by an improper reaction of the binder probably related to the applied water amount. Therefore, additional tests were conducted, in which the water amount was designed to assure a full reaction of the binder. The results of this treatment led to boards with bending and compressive strength properties presented in Figure 1.16. The results show a clear separation in density of the increased binder amount. The strength properties show that the increased binder amount leads to a higher compressive strength, but does not significantly contribute to an increased bending strength. Therefore, an evaluation of the stress and strain curves of the tested boards is performed of which some curves are presented in Figure 1.17. It is revealed that the behavior of the composite is altered by the modification of the binder amount. By the increased binder amount the strain reduces since the wood wool strands become less flexible and will therefore contribute less to the composite properties. Hence, with the higher binder amount the applied load can be higher before a board breaks. However, a rapid failure of the test specimens occurs when reaching the breaking point, while with a lower binder amount the maximum load is lower and the boards first deform.
Figure 1.15: (a) Compressive strength and (b) Bending strength of 1.5 mm WWCB produced with higher binder amounts (HB) and lower binder amounts (LB).

Figure 1.16: (a) Compressive strength and (b) Bending strength of water-pretreated 2.0 mm WWCB with higher binder amounts (HB) and lower binder amounts (LB).

Figure 1.17: Stress strain curves of (a) Compressive and (b) Bending strength of water-pretreated 2.0 mm WWCB with higher binder amounts (HB) and lower binder amounts (LB) and a water-pretreatment.
1.5 Developments in WWCB

So far only boards are introduced, with consisting of wood wool strands covered with cement. However, since the start of WWCB production, the industry is seeking for utilization opportunities and the market needs introducing additional products like reinforced WWCB, sandwich boards and large WWCB elements.

Reinforced WWCB consist of 3 rectangular hardwood slates of 20 x 20 mm² placed at a distance of 150 mm in a board of 600 mm. The slates increase the bending strength providing an additional load bearing capacity and can be applied on ceilings in garages and as roof covering. The benefit of this material is its high thermal capacity that reduces the fluctuations of room temperatures in summer time. To fulfill the demand of thermal insulation, sandwich boards are introduced (Figure 1.18) consisting of an WWCB layer on which PIR, EPS, XPS, mineral wool or PF (resole foam) can be attached.

![Image of WWCB ingredients and boards combined with EPS and mineral wool.](www.eltomation.com)

**Figure 1.18:** WWCB ingredients and boards combined with EPS and mineral wool. Illustration taken from www.eltomation.com with approval of van Elten (2006).

Nowadays, the production of a wood wool strands cement walls with a thickness up to 0.4 m has been successfully executed (van Elten, 2008). This large WWCB element has dimensions of 2.8 x 6.0 x 0.4 m³ (H x W x D) with a density of 330-350 kg/m³ (van Elten, 2015). This type of product provides thermal insulation values (Re) of ~5 m²K/W with a thermal conductivity (λ) of 0.08 W/mK. The product is interesting because it consists of locally available raw ingredients (wood, cement and water) (Ashori et al., 2011) and its resistance against termites (Eusebio et al., 2000).

1.6 Conclusions

The production of wood wool strands cement boards is extensively discussed in this Chapter, giving an overview on the complexity of the boards and their properties. During production, many parameters are influencing the final product like the storage conditions, used knives, recipes and material dosage. Overall, moisture is in all stages a very influential parameter, which is practically difficult to control in the current production process. Moreover, the raw materials cement and wood are addressed, indicating the importance to lower the environmental footprint of the boards and providing insights in the basic wood structure. Based on the study, the following conclusions can be drawn:
• The moisture content ($Mc$) of the wood logs together with the density of the wood-logs in terms of dry-mass, have a significant effect on the industrial production of WWCB. They influence not only the life time of cutting knives and energy consumption of the wood wool strands shredding machines, but also the dimensions of the produced wood wool strands. It is recommended that the $Mc$ of the wood-logs for board production is in the range of 20-35% based on oven-dry wood.

• By dividing wood-logs in different density classes, and shredder the low density wood-logs with a proper moisture content, the lifetime of knives in the shredding machine can be prolonged and the deviation in the dimensions of wood wool strands can be minimized.

• The defined ratio between wood + moisture and binder amount is found to be successfully utilized in the production process. However, since the moisture and wood amount in the parameter wood + moisture is fluctuating, no clear relation could be described between the three ingredients and the final board properties. This while the influence of a higher binder amount or lower wood volume has significant impact on the final board properties.

• In case of applying a higher binder amount, application of sufficient water is of high importance, to obtain boards with the required properties.

• Compatibility between wood and cement is still a studied matter, as well as the use of alternative binders in combination with wood. The use of alternative binders is by its low environmental footprint worth researching.

• The total water demand required for WWCB during the industrial production can be divided into: (1) the moisture to reach the saturation point of the used wood (30% of the dry oven mass); (2) the water demand that cement particles can absorb from the wood wool to fully react; the later depends on the cement type.

1.7 Problem statement

Retardation effect

Although the background study reveals that wood cement products are used for centuries, the combination is not as straightforward because of the interaction mechanism between the wood and cement leading to a postponed hardening of cement known as the retardation effect. The mechanism of retardation on cement, was extensively studied in the 1970’s and 1980’s (Yamamoto, 1972; Young, 1972; Popovics, 1976; Milestone, 1977; Thomas and Birchall, 1983), although still not fully understood. Nevertheless, a common solution to prevent retardation is by using accelerators like Na$_2$SiO$_3$, CaCl$_2$ and MgCl$_2$ (Hachmi et al., 1990; Simatupang and Geimer, 1990; Jorge et al., 2004; Pereira et al., 2006; Fan et al., 2012). However, the use of chlorides for WWCB is restricted by EN 13168 in which specifications are provided regarding factory made wood wool products.

Environmental footprint

Despite the advantageous application of cement in lignocellulosic composites, the increasing worldwide awareness of the substantial contribution of Portland cement (PC)
to greenhouse gas emissions (Florea et al., 2014; Ramezanianpour, 2014) results in searching for alternative materials and development of new binders (Pacheco-Torgal et al., 2008, 2012; Provis, 2014). The design of lignocellulose composites with alternative binders potentially have environmental and economic advantages e.g. reduction of CO\textsubscript{2} emissions and raw materials that go to landfill as well as lower costs (van Elten, 2015). As of today, supplementary materials like limestone powder, fly ash or ground granulated blast furnace slag are commonly used as cement replacement. Nevertheless, studies also reveal that higher substitution levels drastically influence the early strength development of the binders. Therefore, the addition of alkalis to enhance the dissolution of the supplementary materials has been introduced that allows full replacement of cement (Yang et al., 2013; Ouellet-Plamondon and Habert, 2015). However, the question remains if alkali activated binders can be used with wood wool since the exposure of lignocellulose in an alkaline environment initiates several reactive phenomena, e.g. dissolution of organic acids, polysaccharides, peeling reactions, hydrolysis of glycosidic bonds and acyl groups (Mirahmadi et al., 2010).

**Board properties**

Depending on the used binder, the chemical composition and internal structure of the reaction products differ. Therefore, the material properties of the composite can vary distinctively when different types of binders are used (Reinhardt, 1998; Pacheco-Torgal et al., 2008; Ramezanianpour, 2014). Moreover, due to new production techniques and material innovations, competitive materials are rapidly entering the market while the acceptance of a material is defined by its ability to satisfy multiple requirements. A material with a range of contributions results in more suitable product for various conditions and special applications. To stay competitive, clear insight in WWCB properties is needed that allows a tailor-made WWCB.

### 1.8 Research targets

**Objectives and methodology**

The research is carried out by performing a systematic study to address the above stated challenges and provides solutions that can be directly applied in practice. This study is performed in close cooperation with the companies Knauf Insulation, Eltamation, ENCI and Van Gansewinkel Minerals to provide information which is not addressed in literature. Overall, this thesis provides some insights in the influential parameters during production, reaction mechanisms of applied binders, microstructural adjustments that alter the board properties and disposal and reuse of WWCB after its lifetime. The thesis consists of three core elements, whose objectives and methodology are provided in the following sections.

**Part I: Binder**

The objective of the first part of this thesis is twofold (1) reducing the retardation effect by sugars and (2) reduction of the environmental footprint of wood wool composites which both are connected to the applied binder.
To investigate the retardation mechanism of wood on cement hydration, a simplified method by using glucose is applied. The retarding effect on several cement phases is measured to indicate to which extent C₃A and C₄AF with varying anhydrite percentages is affected, with the aim to reduce the retardation on the calcium silicate hydrates. By using an isothermal calorimeter with different Portland cement types, clinkers and additions of glucose, the heat release of the mixtures is analyzed. The reaction product in the form of portlandite is then further analyzed at different hydration times by Thermal Gravimetric Analysis (TGA) and the microstructure was analyzed by Scanning Electron Microscope (SEM). Finally, mortars and wood cement composites are created to validate the present findings.

The objective of the reduction of the environmental footprint is divided into (i) application of Papersludge fly ash (PsFA) to WWCB and implementation of an optimized mix design to determine the rate of cement replacement and influence on the board properties (ii), to evaluate the mechanism occurring when an alkali activated binder is used in the presence of wood, and to define the pre-treatment needed to reduce the liquid uptake by the hygroscopic behavior of wood.

For the application of PsFA, two treatment pathways are evaluated to increase the usability of supplementary cementitious materials (SCMS), in this case, industrially calcined PsFA by reducing its water demand. The PsFA, both treated and untreated, are physically and chemically characterized. By monitoring the heat release, the reactivity of the binder is examined. The suitability of PsFA as a cement substitution is then evaluated, by producing wood wool composites and defining the influence on the properties such as thermal insulation and sound absorption.

Furthermore, an eco-friendly binder is designed with not a porous matrix but a matrix with lower amount of voids optimizing the theoretical particle packing density of the binder by using the modified Andreasen and Andersen model.

For the alkali activated binder, the wood behavior under alkaline conditions is first evaluated by pH measurements together with the reaction mechanism of the studied binders using an isothermal calorimeter. Next, the ionic behavior of Ca²⁺ and Na⁺ in the absence and presence of wood is studied using an ion-chromatography. Furthermore, the location of liquid water using NMR in wood is studied. The obtained knowledge led to the design of a sustainable lignocellulosic mineral-binder composite using different alkali activated binders.

**Part II: Development of board properties**

The objectives of the second part of this thesis is twofold: (1) to evaluate the suitability of WWCB to be used as an air purifying material by implementing a photocatalytic coating and to determine the influence of the surface structure of the board and (2) to model the sound absorption of WWCB, by defining the required input parameters and studying the influence of WWCB parameters on the sound absorption.

To increase the functionality of the board by addressing the indoor air purification of WWCB, a photo-catalyst, titanium dioxide (TiO₂), is applied on different WWCB with various surface structures and binders. Using a mixture of NO and NO₂ as the target pollutants the degradation rate of these pollutants is investigated under different airflow to evaluate the influence of surface structure and binder type. Moreover, a durability study is conducted exposing boards to steady and dynamic water treatments.
To model the sound absorption of WWCB, first commercially available WWCB are measured using an impedance tube and the required input parameters are obtained by using the curve fitting approach. By using multiple samples with a variety of densities and using 1.0, 1.5 and 2.0 mm strand widths the most accurate model is selected for further use. The selected impedance model is then demonstrated using different strand widths and board thicknesses. Afterwards, the influence of board ingredients and properties like strand width, density, wood to binder ratio, moisture content, board thickness and application of an air cavity are studied together followed by an optimization study with extrapolating the obtained parameter functions.

Part III: Disposition and Reuse of WWCB

The objective of the third part of this thesis is to investigate the disposition of WWCB after its service life following the waste hierarchy from re-use to disposal at landfill sites. Although this part is closely related to Part I, with the aim to reduce the environmental footprint, it focusses less on implementation of a binder and board properties (Part II) and more on the method to reuse minerals classified as unsuitable for reuse (waste). It is found that a common end step after the service life of WWCB is energy recovery by incineration. However, due to the large volume required for the incineration and the relative small waste volume of WWCB, the waste is often mixed with other wood products which are more contaminated, hence, it generates contaminated fly ashes. Therefore, four different fly ash types produced by two different biomass incineration plants were analysed and compared to Dutch and European standards on building materials. A combined treatment method was designed for lowering the leaching of contaminants and the effect of each treatment step was quantified. Finally, a pilot test was performed in order to scale up the treatment and make the biomass fly ashes suitable to be used as SCM.

1.9 Outline of this thesis

This research is based on multidisciplinary approaches and aims to provide insight into development of novel WWCB products that are environmentally friendly and widely applicable. Although WWCB is known since 1920, to the authors knowledge, there are only a handful of papers available on this topic. Knowledge of application of alternative binders in other materials, e.g. binders in concrete products, is used in this study. Also, application of widely used acoustic impedance models is applied to WWCB to identify the acoustical properties of boards with different physical properties. Moreover, the application of a photocatalyst and its influence on material air purifying properties is studied. The research framework of this thesis is presented in Figure 1.19.

Chapter 1 is an introduction to WWCB, briefly addressing the ingredients, the production process and resulting board properties of commercial WWCB, introducing influential parameters and the complex interaction between the wood wool strands and binder. These results are obtained in the real scale production of WWCB. After that, the core of the thesis is organized into three parts, composed by self-contained chapters:

- Part I, composed by Chapter 2, Chapter 3 and Chapter 4, describes different approaches to optimize the used binder and the application of alternative binders
to reduce the environmental footprint of the boards. Chapter 2 presents the study on hydration of cements and the retardation of sugars on cements with varying aluminate and CaSO₄ contents providing new insights to the retardation mechanism and a novel solution to reduce the retardation effect. Chapter 3, describes the implementation of PsFA as a supplementary material leading to increased mechanical and thermal properties and a reduced environmental footprint. In addition, densification of the binder matrix by optimizing the particle packing is evaluated. Chapter 4 describes the use of alkali-activated binders, to fully replace cement, identifying the alkaline degradation mechanism of wood and reaction mechanisms which have not been studied before for such system (mineral binder combined with wood wool). The study lead to the development of a hybrid binder that results in a carbon footprint reduction of 60% compared to the use of cement as binder and leads to significant reduction in costs.

- Part II, composed by Chapter 5 and Chapter 6, describes different approaches to optimize the board performances. Chapter 5, describes a method to increase the functionality of the boards by implementation of a photocatalytic coating. The study leads to increased insights in the surface influence and ultimately in a high efficiency of 98% (according to the knowledge of the author such values have not been reported before) in air purification using WWCB. Chapter 6, describes an approach to model the sound absorption of WWCB. Different commercial WWCB are characterized and, by using impedance models, the sound absorption of WWCB are predicted with varying strand widths, densities, thicknesses and air cavities providing new insights in the acoustic behavior of WWCB and enabling the enhancement of the sound absorbing properties by increased densities and multilayer constructions.

The content of the chapter is almost identical to the published article (Botterman et al., 2016). The experimental and modeling work is conducted by Bram Botterman and is part of his master thesis (Botterman, 2016). During his study I was his daily supervisor and we performed the research and analyzes together. Our collaboration of 1.5 years was followed by his graduation, and we continued to work together on writing the journal article (Botterman et al., 2016), on which this chapter is based on.

- Part III, Chapter 7, considers the disposition of commercial WWCB after its service life time and leaded to waste wood incineration and contamination of residues that required the design of economical feasible treatments not seen before. Moreover the designed treatment is evaluated on a pilot scale, resulting in a binder which could re-enter the market as a SCM.

In Chapter 8, comprehensive conclusions of the present work are drawn and recommendations for future research are provided.
Figure 1.19: Schematic presentation of the thesis outline.
Chapter 2

Hydration kinetics of cement containing sugars


2.1 Introduction

The mechanism of retardation on cement by organic compounds has been known for years, relating to a wide range of applications such as wood cement composite boards (Aggarwal and Singh, 1990; Aggarwal et al., 2008), the utilisation of by-products containing organics to partially replace cement (Doudart de la Grée et al., 2016; Tang et al., 2015), the application of organic fibres in concrete (Cheah and Ramli 2011), and the use of retarding admixtures in concrete (Abalaka, 2011; Taylor, 1990; Ramachandran and Lowery, 1992). In the case of admixtures, the retardation leads to a favourable condition by delaying the setting time of the cement (Neville, 2002; Hewlett, 2004; Huang and Shen, 2014; Cheung et al., 2011a). In the other above-mentioned applications, the retardation is often seen as negative and not desired due to the reduced early stage mechanical properties or even termination of the cement hydration. Therefore, additives such as Na_2SiO_3 or CaCl_2 are added (Lee, 1984), although the latter is restricted to wood cement composite boards (Lee and Short, 1989; Mencnarowski, 2014).

Studies have been extensively conducted in the last centuries on the retarding mechanism of organic admixtures on Portland cement (Young, 1972; Lieber and Richartz, 1972; Yamamoto, 1972; Singh, 1975; Milestone, 1977; Thomas and Birchall, 1983; Collepardi et al., 1984; Yang and Montgomery, 1996; Ramachandran, 1996; Ramachandran and Lowery, 1992; Abalaka, 2011; Bishop and Barron, 2006; Huang and Shen, 2014). An increased dissolution of Ca, Si, Al, Fe, and OH\(^{-}\) was found when Portland cement was mixed with a solution containing sugars (e.g., sucrose of 15 mM). Depending on the type of sugar, the solubility degree of cement was altered, separating the weak retarders from the strong (Thomas and Birchall, 1983). Subsequently, the actual retardation of the cement compounds started, which can be described by different processes occurring simultaneously, namely adsorption, precipitation, complexation, and nucleation control (Young, 1972). The fast hydration of the compounds C_3A and C_3S led to an increased alkaline environment, which interacts with the glucose molecules by the following mechanisms: (1) electrostatic interaction, (2) ring opening, and (3) the degradation of glucose resulting in more than 50 products (Yang and Montgomery, 1996), mainly acids (Shaffer and Friedemann, 1929; Nef, 1913), capable of forming complexes with cations by acting as a ligand. This consequently favours the Ca (Bishop and Barron, 2006), Al, and Fe chelating complexations (Thomas and Birchall, 1983; Young, 1972) that arise with organic compounds containing one or more oxy-functional groups (Taplin, 1962).
Furthermore, complexation production can also precipitate on the hydration products depending on their solubility. There they poison the calcium silicate nucleation sites by (1) changing the zeta potential from a positive to a negative charge (Ramachandran, 1996) and (2) forming insoluble metal organic complexes, which coat the clinker phases (Suzuki and Nishi, 1959). Because of the unavailability of the ions and retardation of the hydration products from the aluminate phases, a lower amount of portlandite could be detected. A schematic overview of the inhibitory effect of glucose on cement hydration is given in Figure 2.1.

Numerous researches have investigated the effects of organic compounds on the setting and early hydration of various cement phases, including C$_3$A since it is the fastest reacting phase and C$_3$S since it is the phase that dominates the early strength development (Young, 1972). In the presence of C$_3$S, the effect of C$_3$A is the removal of the admixture from the solution, thereby preventing a strong retarding effect on C$_3$S (Young, 1972). Cheung et al. (2011b) reported the importance of supplying sulfate to balance the cement admixture response. Problems with silicate phase hydration in the presence of admixtures can be traced to inadequate control of the aluminate phase hydration by the sulphate present in cement (Sandberg et al., 2007; Perez and Sorrentino, 2007). Since sulphate content will influence the reaction products of the aluminate clinker phases, it also interferes in glucose’s interaction with the aluminate phases. Hence, less glucose will interact with the aluminate phases and, therefore, a higher glucose content will start influencing the C$_3$S reaction.

In this study, the hydration kinetics of cement containing sugars was investigated, with the aim of understanding the cement hydration behaviour in an organic environment (e.g., in the scenario of wood cement composites or wood particle boards), where an inhibitory of the cement hydration can cause significant production difficulties (Mencnarowski, 2014; van Elten, 2015). Two widely applied Portland cements, namely white and grey cement, were investigated. Because of the complex chemical composition of wood and the resulting complex organic behaviour, multiple reactions occur by numerous components simultaneously. In this study, the system was simplified by only using glucose as a retarder so that observed reactions could be more easily interpreted. Moreover, glucose in concentrations of 0.05-0.3% is often used (Collepardi et al., 1984; Huang and Shen, 2014; Singh, 1975; Young, 1972; Reinhardt, 1998; Ramachandran, 1996; Cheung et al., 2011b) in cement chemistry and wood cement composite science research (Jorge et al., 2004; Simatupang and Geimer, 1990) because of its retardation mechanism.

The effect of the CaSO$_4$ dosage and glucose concentration on the cement hydration kinetics was investigated by using an isothermal calorimeter. The hydration product in the form of portlandite was then further analysed at different hydration times by thermal analysis and XRD. Furthermore, CSH gel formation was evaluated by FTIR, and the microstructure was analysed by SEM. Subsequently, mortars and wood cement composites were created to validate the findings of the study, revealing a reduced retardation in the cases of grey cement with 7% CaSO$_4$ and white cement with 4% CaSO$_4$ content.
2.2 Materials and Methods

2.2.1 Materials

Two types of Portland clinkers (ENCI, NL) were studied with the following CaSO\(_4\) ratios: 0, 2.5, 4.0, 5.0, 6.0, and 7.0% by mass of clinker. The clinkers have the same Blaine surface area compared to the samples containing 5% CaSO\(_4\), which are commercially available as CEM I 52.5 R and CEM I 52.5 R White cements (ENCI, NL), termed G and W, respectively. The chemical compositions of the two cements determined by X-ray fluorescence (XRF), together with the main cement phases calculated by using the commonly applied Bogue equations (Crumbie et al., 2006; Shanahan and Zayed, 2007), are presented in Table 2.1.

Table 2.1: Chemical composition and main compounds in which G and W stands for CEM I 52.5 R and CEM I 52.5 R White.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>G [%]</th>
<th>W [%]</th>
<th>Phases</th>
<th>G [%]</th>
<th>W [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>63.71</td>
<td>67.19</td>
<td>C(_3)S</td>
<td>56</td>
<td>80</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>20.27</td>
<td>20.86</td>
<td>C(_2)S</td>
<td>17</td>
<td>0</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>4.80</td>
<td>3.91</td>
<td>C(_3)A</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>3.43</td>
<td>0.45</td>
<td>C(_3)AF</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>SO(_3)</td>
<td>2.91</td>
<td>2.92</td>
<td>C(_5)S</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

The physical properties such as BET specific surface area, particle size distribution, and specific density were measured by using a Micrometrics Tristar II 3020 with N\(_2\) adsorption, a Malvern Mastersizer 2000, and an AccuPyc 1340 II gas Pycnometer, respectively. G has a BET surface area of 1.50 m\(^2\)/g, a mean particle size d\(_{50}\) of 14.44 μm, and a specific density of 3150 kg/m\(^3\), whereas W is a bit coarser with a BET surface area of 1.21 m\(^2\)/g, a mean particle size d\(_{50}\) of 16.90 μm, and a specific density of 3106 kg/m\(^3\). Compared to G, W has a higher C\(_3\)A content (~ 3%) and a higher C\(_3\)S content (~ 20%), while having a similar gypsum content (both ~ 3%).
D-glucose (Merck KGaA) was used as retarder in the present study. Two different dosages of 0.2 and 0.3% by mass of cement, corresponding to a \((\frac{C_3A + C_4AF}{\text{glucose}})\) ratio of 1.17% and 1.76% for G and 1.81% and 2.72% for W, were applied to investigate the dosage effect. Wood wool cement boards (WWCB) were studied to validate the present findings. The choice of producing this type of board was threefold. Firstly, this type of board normally consists of a high bulk volume of wood compared to the volume of binder (wood volume to binder volume ratio of 5.5 for a board density of 450 kg/m\(^3\)), leading to a thin layer of 40-140 µm of binder on the wood wool (Doudart de la Grée et al., 2014) and, therefore, a potentially large influence on the binder hydration mechanism. Secondly, during the production process of WWCB, the wood is first wetted and later sprinkled with cement. During the mixing, the water within the wood is taken up by the cement together with extractives that can interfere with the cement reaction. Thirdly, after casting to moulds, the boards are pressed for 24 h. The cement needs to be sufficiently hardened within this period to ensure a dimensionally stable board; otherwise, the matt of wood wool covered by cement will swell, resulting in a loosely packed composite with very poor properties.

The spruce wood wool used in this study had a width of \(\sim 1.5\) mm, a thickness of \(\sim 0.24-0.35\) mm, and a length of \(\sim 25\) cm. Both the bulk and specific densities of the wood wool were determined by mercury porosimetry using a Micromeritics AutoPore IV 9500, namely 761 kg/m\(^3\) and 1345 kg/m\(^3\), respectively, yielding a porosity of 63.85%. The chemical composition of the wood was determined by using different techniques. The acid insoluble lignin was determined according to Tappi T222 (Tappi Method T 222 om-88, 1988), and the acid soluble lignin according to Tappi UM250 (Tappi Method UM 250, 1985). The extractives were determined according to Tappi T264 (Tappi T264 om-88, 1996). The polysaccharides, hemicelluloses, and cellulose were determined by acid hydrolysis using a high performance anion exchange chromatograph (HPAEC). Table 2.2 presents the chemical composition of the wood. Glucose is the major sugar, along with Arabinose, Xylose, Rabmose, Mannose, and Galactose. Reported literature indicated a slightly higher glucose content ranging between 41.5% (Tjoelker et al., 2007) and 45.5% (Bertaad and Holmbom, 2004) for Norway spruce. All of the sugars, including glucose, belong to the class of reducing sugars that are prone to ring opening and degradation under the alkaline environment (Bishop and Barron, 2006). This reflects the validity of using glucose as a representative to study the cement hydration kinetics containing wood.
Table 2.2: Chemical composition of the used spruce wood in [%] (Merta, 2014).

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

2.2.1 Experiments

To study the hydration kinetics, a series of mixtures listed in Table 2.3 were tested by using a TAM AIR isothermal calorimeter. The heat release was recorded for 90 h with a water to powder ratio of 0.5 under a fixed temperature of 20 °C to focus on early age behaviour. The default glucose content in this study was 0.2 wt.% of cement. Furthermore, a glucose content of 0.3 wt.% of cement was used to investigate the reaction mechanism when a prolonged retardation was expected due to the higher glucose amount. The powder samples were first transferred in an ampoule and then well mixed before water was added. After the addition of water, the mixture was mixed for 2 min and the ampoule was loaded to the isothermal calorimeter. The heat evolution data were calibrated by subtracting the heat evolution of ampoules with water as a baseline.

The thermal mass loss between 400 and 500 °C was used to estimate the Ca(OH)$_2$ content (Shui et al., 2008; Alonso and Fernandez, 2004; Zhang and Ye, 2012). Minor mass loss due to the loss of the chemically bound water in CSH in this range was neglected (Khoury et al., 2002). First, the mass of the empty crucibles was determined after pre-heating at 600 °C and cooling down until reaching ambient laboratory temperatures of 20 °C. The crucibles were then filled with the samples and oven dried at 105 °C until the mass was constant. Subsequently, the samples were heated at 400 °C for 18 h following the same procedure and finally heated at 500 °C.
Table 2.3: Tested recipes in which G and W stands for CEM I 52.5 R and CEM I 52.5 R White.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Portland cement type</th>
<th>Glucose (wt. % cement)</th>
<th>CaSO4 (wt. % cement)</th>
<th>glucose / (C3A + C4AF) [%]</th>
<th>CaSO4 / (C3A + C4AF) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>G</td>
<td>0</td>
<td>5.0</td>
<td>0</td>
<td>0.294</td>
</tr>
<tr>
<td>2</td>
<td>G</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>G</td>
<td>0.2</td>
<td>5.0</td>
<td>1.17</td>
<td>0.294</td>
</tr>
<tr>
<td>4</td>
<td>G</td>
<td>0.2</td>
<td>-</td>
<td>1.17</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>G</td>
<td>0</td>
<td>4.0</td>
<td>0</td>
<td>0.235</td>
</tr>
<tr>
<td>6</td>
<td>G</td>
<td>0.2</td>
<td>4.0</td>
<td>1.17</td>
<td>0.235</td>
</tr>
<tr>
<td>7</td>
<td>G</td>
<td>0</td>
<td>2.5</td>
<td>0</td>
<td>0.147</td>
</tr>
<tr>
<td>8</td>
<td>G</td>
<td>0.2</td>
<td>2.5</td>
<td>1.17</td>
<td>0.147</td>
</tr>
<tr>
<td>9</td>
<td>G</td>
<td>0.2</td>
<td>6.0</td>
<td>1.17</td>
<td>0.353</td>
</tr>
<tr>
<td>10</td>
<td>G</td>
<td>0.2</td>
<td>7.0</td>
<td>1.17</td>
<td>0.412</td>
</tr>
<tr>
<td>11</td>
<td>G</td>
<td>0.3</td>
<td>5.0</td>
<td>1.76</td>
<td>0.294</td>
</tr>
<tr>
<td>12</td>
<td>G</td>
<td>0.3</td>
<td>4.0</td>
<td>1.76</td>
<td>0.235</td>
</tr>
<tr>
<td>13</td>
<td>G</td>
<td>0.3</td>
<td>6.0</td>
<td>1.76</td>
<td>0.353</td>
</tr>
<tr>
<td>14</td>
<td>W</td>
<td>0</td>
<td>5.0</td>
<td>0</td>
<td>0.455</td>
</tr>
<tr>
<td>15</td>
<td>W</td>
<td>0</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>W</td>
<td>0.2</td>
<td>5.0</td>
<td>1.81</td>
<td>0.455</td>
</tr>
<tr>
<td>17</td>
<td>W</td>
<td>0.2</td>
<td>-</td>
<td>1.81</td>
<td>-</td>
</tr>
<tr>
<td>18</td>
<td>W</td>
<td>0</td>
<td>4.0</td>
<td>0</td>
<td>0.364</td>
</tr>
<tr>
<td>19</td>
<td>W</td>
<td>0.2</td>
<td>4.0</td>
<td>1.81</td>
<td>0.364</td>
</tr>
<tr>
<td>20</td>
<td>W</td>
<td>0</td>
<td>2.5</td>
<td>0</td>
<td>0.227</td>
</tr>
<tr>
<td>21</td>
<td>W</td>
<td>0.2</td>
<td>2.5</td>
<td>1.81</td>
<td>0.227</td>
</tr>
<tr>
<td>22</td>
<td>W</td>
<td>0.3</td>
<td>5.0</td>
<td>2.72</td>
<td>0.455</td>
</tr>
<tr>
<td>23</td>
<td>W</td>
<td>0.3</td>
<td>4.0</td>
<td>2.72</td>
<td>0.364</td>
</tr>
</tbody>
</table>

X-ray diffraction (XRD) measurements were performed on selected samples, using a Rigaku Geigerflex X-ray diffractometer with Cu-radiation and a detection angle between 15 and 60° to study the hydration products with a primary focus on the crystalline portlandite. A PerkinElmer Frontier™ MIR/FIR Spectrometer using the attenuated total reflection (ATR) method (GladiATR), 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹, was used to analyse the CSH structure, which was typically shown at around 950 cm⁻¹. The microstructure was visualised by using scanning electron microscopy (SEM) at high vacuum conditions. The evaluated samples were first oven dried at 30 °C for 24 h.

To investigate the performance of the studied systems, mortar samples with a w/b ratio of 0.5 were prepared using a laboratory mixer. The solid materials were added into the mixer followed by the prepared glucose solution. The fresh mortar was cast into moulds of 40 x 40 x 160 mm³ and vibrated. Finally, all specimens were demoulded and cured at 20 °C with a relative humidity of 95%. Flexural and compressive strength tests were carried out according to EN 196-1 at the ages of 1, 2, 3, 7, and 28 days.

The WWCB were produced using the following recipe and preparation procedure. A total water to powder ratio of 1.0 and a wood to powder ratio of 0.75 by mass of cement was used (Doudart de la Grée et al., 2014). The target density of the boards was 450 kg/m³. Firstly, for the pretreatment of the wood, water was applied, corresponding to 30% of the dry mass of wood. Secondly, the binder was mixed with the wet wood wool for approximately 30 sec. Next, the wood wool cement composite was transferred into a mould with a size of 30 x 50 cm² (W x L). Subsequently, the mould was removed, and
the composite was sealed and compressed to the desired height by using distance holders of 15 mm. After 24 h of compression, the boards were stored for 10 days under ambient conditions. Finally, the boards were dried in an oven at 100 °C for 2 h to remove the remaining capillary water, and three samples of 15 x 20 cm² (W x L) were extracted from one board. The apparent density of the boards was determined by the measured mass and bulk volume. The flexural strength was measured by using a tree point bending flexural test instrument in accordance with EN 12089.

2.3 Results and discussions

2.3.1 Hydration kinetics of cements/clinkers without glucose

Figure 2.2 illustrates the heat evolution and heat flow rates of both G with 5% CaSO₄ (Mix 1) and W with 5% CaSO₄ (Mix 14), in the first 90 h of hydration. Two or three distinguishable peaks were observed in Mix 1 and Mix 14, as presented in Figure 2.2b. The first sharp peak was attributed to the dissolution of particles and fast reaction of Ca₃A that reacts with Ca²⁺ and SO₄²⁻ ions, yielding the formation of calcium sulfo aluminate hydrates in the form of \((\text{Ca}_6\text{Al}_3(\text{SO}_4)_3(\text{OH})_{12}, 26\text{H}_2\text{O})\) (Taylor, 1990) and hydroxy–AFm (Pourchet et al., 2009). This product precipitated on the cement particle surface and eventually together with other reaction products slowed down the hydration of C₃A. C₃A hydrates around 5-25% in the pre-induction period (Taylor, 1990). The hydration of C₃A with gypsum and water formed calcium sulfoaluminate hydrate, ettringite, reading:

\[
\text{C}_3\text{A} + 3\text{CSH} + 26\text{H} \rightarrow \text{C}_6\text{A}\text{S}_3\text{H}_{32}
\]  

(2.1)

When all the gypsum in the cement was consumed by the reaction with C₃A, the remaining C₃A dissolved until the solution becomes supersaturated with respect to calcium aluminate monosulfate, which then precipitated together with other amorphous phases (Cuesta et al., 2015; Minard et al., 2007).

C₃S reacted in the pre-induction period in small quantities, yielding CSH gels and contributed together with the C₃S to the Ca²⁺ and OH⁻ concentration in the liquid phase. The second peak attributed to the reaction of C₃S and the second stage CSH starts to be formed. CaSO₄ became completely reacted and the concentration of SO₄²⁻ ions started to decline, due to the formation of the AFt phase. Finally, in case of Mix 14, a third peak appeared due to a second stage reaction of C₃A (at 18 h) when all the gypsum was consumed, leading to the precipitation of calcium hydroaluminates consuming calcium ions and releasing from the aluminium ions in solution (Minard et al., 2007). The higher the gypsum content, the longer it takes for the gypsum to be fully consumed and the later the third peak occurs (Minard et al., 2007; Quennoz and Scrivener, 2012). The reaction of C₄AF was essentially similar to that of C₃A (Chatterji and Jeffery, 1962) in the presence of SO₄²⁻ ions, forming calcium sulfoaluminate hydrates and calcium sulfoaluminoferrite hydrates in a second stage reaction when all the gypsum is consumed, forming calcium (aluminate, ferrite) monosulfate (AFm) (Cuesta et al., 2015; Fukuhara et al., 1981).
Chapter 2

Figure 2.2: (a) Normalized heat; (b) Normalized heat flow of G with 5% CaSO₄ (Mix 1), G with 0% CaSO₄ (Mix 2), W with 5% CaSO₄ (Mix 14) and W with 0% CaSO₄ (Mix 15).

The thermal analysis presented in Figure 2.3 displays an increasing amount of portlandite in the early age reaction (20,72 h) which is attributed to the reaction of C₃S, following (A. Neville, 2002):

\[ 2C₃S + 6H \rightarrow C₃S₂H₃ + 3CH \]  \hspace{2cm} (2.2)

However, according to Taylor (Taylor, 1990), the hydration of C₃A in time is to a high degree delayed by the reaction with CaSO₄, and it is also delayed in the presence of a high quantity of portlandite. Therefore, consumption of portlandite occurs by the reaction of C₃A (Ramachandran, 1996; Taylor, 1990), as:

\[ C₃A + CH + 18H \rightarrow C₄AH₁₉ \]  \hspace{2cm} (2.3)

and in case C₄AF (Neville, 2002), as:

\[ C₄AF + 2CH + 10H \rightarrow C₃AH₆ + C₃FH₆ \]  \hspace{2cm} (2.4)

Figure 2.3: Estimated portlandite amount for G with 5% CaSO₄ (Mix 1), G with 0% CaSO₄ (Mix 2), W with 5% CaSO₄ (Mix 14) and W with 0% CaSO₄ (Mix 15), at 20 and 72 h of hydration.
In both $G$ and $W$ with 0% CaSO$_4$ (Mix 2 and Mix 15), the heat evolution in the first 30 min was 20 and 33 J/g, respectively, and was significantly higher compared to the Mix 1 and Mix 14 with 5% CaSO$_4$ (7.5 and Mix 8.0 J/g), as presented in Figure 2.2. This is mainly due to the reaction of C$_3$A forming calcium aluminate hydrates. The difference in the heat release between $G$ and $W$ is related to the higher quantity of C$_3$A present in $W$. The heat release of Mix 2 rapidly increased for 9 h, which is attributed to the reaction of aluminate phases C$_3$A and C$_4$AF. The results indicate that the reaction continued and was not retarded by the hydration products covering the cement particles. Taylor (Taylor, 1990) mentioned a similar behaviour, stating that the reaction of C$_4$AF in the presence of high amounts of portlandite can be slowed down. Mix 15 showed, after the pre-induction period, a gradual increase of heat up to 24 h, and no third peak was observed due to the absence of CaSO$_4$. The initial increase of heat is attributed to the reaction products from C$_3$A corresponding to the phases C$_2$AH$_x$ and C$_4$AH$_x$ that ultimately converted to a more stable hydrate C$_3$AH$_x$ (Taylor, 1990). Because of the reaction of C$_3$A and initial dissolution of C$_3$S that precipitates on the cement particle surface, the cement hydration was retarded (Taylor, 1990). Therefore, in the case of no CaSO$_4$ being present, the higher the C$_3$A content, the more reaction products precipitated on the cement particles, increasing the retardation.

**Figure 2.4:** XRD pattern showing the main porlandite peaks at $2\theta$ of 18 and 34 for: (a,b) G with 5% CaSO$_4$ (Mix 1); (c,d) for W with 5% CaSO$_4$ (Mix 14) for unreacted (0 h), 20 and 72 h hydrated binder.
The analysis in Figure 2.3 displays an increasing amount of portlandite in the early reaction. With 0% CaSO₄ present, the portlandite amount was lower in both cases compared to the samples with 5% CaSO₄, indicating either a lower initial dissolution of C₃S or lower consumption of portlandite by the reaction of C₃A and C₄AF. The fast hydration of C₃A lead to a lesser formation of portlandite, but in time the amount of portlandite increased due to the reaction of C₃S. The greater amount of C₃S in W compared to G caused the deviation in the amount of portlandite between the samples. The XRD analysis presented in Figures 2.4 and 2.5 confirms the presence of crystalline portlandite in both Mix 1, Mix 14, Mix 2 and Mix 15 at 20 h and 72 h.

![Figure 2.5: XRD pattern showing the main portlandite peaks at 2θ of 18 and 34 for: (a,b) G with 0% CaSO₄ (Mix 2); (c,d) W with 0% CaSO₄ (Mix 15) for unreacted (0 h), 20 and 72 h hydrated binder.](image)

2.3.2 Hydration kinetics of cements/clinkers containing glucose

The heat evolution and heat flow rate of the cements were significantly altered when glucose (C₃A+C₄AF/glucose ratio 1.17% for G and 1.81% for W) was added to the mixtures, as presented in Figure 2.6. Within the first hour, the addition of glucose lead, in the case of W (Mix 16), to a similar heat release as W without glucose (Mix 14), while the initial heat release of G with glucose (Mix 3) compared to G without glucose (Mix 1) was slightly increased by an increased dissolution of C₄AF. Afterwards, the reaction of Mix 3 and Mix 16 were retarded, leading to a very slow increase in heat release until 26 h and
Hydration kinetics of cement containing sugars

43 h, respectively, and then the heat release started to increase dramatically. The variation in heat release between Mix 3 and Mix 16 was mainly due to the difference in chemical composition. \( G \) contains a higher content of \( \text{C}_4\text{AF} \), which with a w/b ratio of 0.4, has an enthalpy of 289 J/g after 3 days of hydration (Taylor, 1990), while \( W \) contains almost no \( \text{C}_4\text{AF} \). In \( G \), \( \text{C}_4\text{AF} \) reacted in the presence of portlandite and \( \text{CaSO}_4 \), slowly forming \( \text{AFt} \) that later was transformed to \( \text{AFm} \), preventing a flash set similar to \( \text{C}_3\text{A} \). Furthermore, the reaction of \( \text{C}_3\text{A} \) with \( \text{CaSO}_4 \) and glucose lead to a thin and impermeable layer of \( \text{AFt} \) (Ramachandran, 1996). In Mix 16, the reaction of \( \text{C}_3\text{S} \) continued, observed by the strength development (as will be discussed in Section 2.3.5), although indicated by a low heat release (enthalpy of 243 J/g (Taylor, 1990)). This was confirmed by the enlargement of the heat release, indicating the main reaction starting from 14 h (Figure 2.6). Therefore, the high heat release of Mix 3 is attributed to the \( \text{C}_4\text{AF} \) reaction, since the other reacting compounds \( \text{C}_3\text{A} \) and \( \text{C}_3\text{S} \) present in \( W \) release a low amount of heat. This is further explained by the heat release of \( G \) with 0% \( \text{CaSO}_4 \) and glucose (Mix 4) and \( W \) with 0% \( \text{CaSO}_4 \) and glucose (Mix 17).

![Figure 2.6](image)

**Figure 2.6**: (a) Normalized heat; (b) Normalized heat flow of \( G \) with 0.2% glucose and 5% \( \text{CaSO}_4 \) (Mix 3), \( G \) with 0.2% glucose and 0% \( \text{CaSO}_4 \) (Mix 4), \( W \) with 0.2% glucose and 5% \( \text{CaSO}_4 \) (Mix 16) and \( W \) with 0.2% glucose and 0% \( \text{CaSO}_4 \) (Mix 17).

It was clearly demonstrated from the heat releases of Mix 4 and Mix 17 that \( \text{C}_3\text{A} \) reacted with glucose, leading to an excessive heat release in the first few hours. In both cases, the dissolution occurred within the first 30 min, yielding a heat release of 29 J/g and 43 J/g for Mix 4 and Mix 17, respectively. Afterwards, less glucose was available to react with other cement compounds, resulting in a very slow increase in heat development for Mix 17. For example, in the case of Mix 4, retardation beyond 90 h was observed due to the lower content of \( \text{CaSO}_4 \) and a reduced reaction of \( \text{C}_3\text{S} \). In the presence of \( \text{CaSO}_4 \), \( \text{C}_4\text{AF} \) formed calcium sulfoaluminoferrite hydrates as well as calcium sulfoaluminate hydrates as:

\[
\text{C}_4\text{AF} + \text{CaSO}_4 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{S}(\text{A}_x\text{F}_y)\text{H}_z
\]

(2.5)

Its presence accelerates the hydration of the silicates (Neville, 2002). In the absence of \( \text{CaSO}_4 \) and increased dissolution of \( \text{C}_4\text{AF} \) by the glucose, the formation of iron-rich gels on the surface of the silicate particles is increased, which is supposed to slow the
hydration of C₃S (Ramachandran, 1996). Together with the fast reaction of C₃A, a fast stiffening of the paste resulted. Furthermore, the amounts of C₃A and C₄AF in G exceed the amount of C₃A in W, resulting in more products precipitated on the other cement compounds. This is supported by the present findings that Mix 16 (containing no C₄AF) was first retarded, but was able to rapidly develop heat when it overcame the retardation after 43 h due to the absence of the iron rich gels, and later even exceeded the heat evolution of Mix 3 at 66 h. The hydration of Mix 17 starts earlier at 33 h compared to Mix 16 because of the incorporation of glucose into the hydration products in the early stage reaction.

Comparing the results presented in Figure 2.7 containing glucose to the results presented in Figure 2.3 without glucose, it is clear that the portlandite amount was significantly lower in all samples. The portlandite amounts in Mix 3 and Mix 16 containing glucose and 5% CaSO₄ followed the same trend as Mix 1 and Mix 14 without glucose and 5% CaSO₄. The same trend is found for the variants Mix 4 and Mix 17 with glucose and 0% CaSO₄, which show a lower amount of portlandite compared to Mix 3 and Mix 16 with 0% CaSO₄. Without CaSO₄, the initial dissolution of C₃S, C₃A and C₄AF reduced, leading to the reduced formation of portlandite. In the presence of glucose, the initial dissolution might be increased, but, afterwards, complexation and reduced reaction of the cement compounds lead in all cases to a reduced formation of portlandite. However, it can be observed that the portlandite amount in case of Mix 17 increased more rapidly compared to Mix 4, which was not observed when having 5% CaSO₄ (Mix 2 and Mix 15). This indicates that the presence of CaSO₄ plays a role in the retardation mechanism. Additional tests using XRD on Mix 3, Mix 4 and Mix 16, and Mix 17 presented in Figures 2.8 and 2.9 confirm a decrease in crystalline portlandite compared to the mixtures without glucose.

**Figure 2.7:** Estimated Portlandite amount for G with 0.2% glucose and 5% CaSO₄ (Mix 3), G with 0.2% glucose and 0% CaSO₄ (Mix 4), W with 0.2% glucose and 5% CaSO₄ (Mix 16) and W with 0.2% glucose and 0% CaSO₄ (Mix 17) at 20 and 72 h of hydration.

Due to the different reaction mechanisms of the cement compounds, the obtained portlandite amount cannot be used as a measure of the calcium silicate hydrate formation, which, therefore, is further evaluated by the strength development as discussed in Section 2.3.5.
Hydration kinetics of cement containing sugars

Figure 2.8: XRD pattern showing the main portlandite peaks at $2\theta$ of 18 and 34 for: (a,b) G with 0.2% glucose and 5% CaSO$_4$ (Mix 3); (c,d) W with 0.2% glucose and 5% CaSO$_4$ (Mix 16) at 0, 20 and 72 h of hydration.
2.3.3 Effect of CaSO₄ content

Starting from the obtained results, investigations were further performed to study the effect of the CaSO₄ dosage, by altering the CaSO₄ content to 2, 4, 5, 6, and 7% by mass of the cement, respectively. The results of the isothermal calorimeter revealed no significant difference in the reaction mechanism of G with 4 and 6% CaSO₄ (Mix 5 and Mix 7) and that of G with 5% CaSO₄ (Mix 1), while the effect of CaSO₄ amount (4 or 6%) was obvious in the case of glucose-contained mixtures (Mix 6 and Mix 9, see Figure 2.10). In the first 30 h, the reactions were similar, but after 30 h the heat release of G with glucose (Mix 3) started to rapidly increase while the heat release of Mix 6 increased at a very low rate. It was shown that a small reduction in the CaSO₄ had a substantial influence on the heat development of G when mixing with glucose, and turned out to increase the retardation. The retardation was even further increased when 2.5% CaSO₄ was used (Mix 8). However, when increasing the CaSO₄ amount to 6%, the retardation was reduced to 23 h and was further reduced to 18 h when 7% CaSO₄ (Mix 10) was applied, showing an incorporation of glucose into the hydration products.

Figure 2.9: XRD pattern showing the main portlandite peaks at 2θ of 18 and 34 for: (a,b) G with 0.2% glucose and 0% CaSO₄ (Mix 4); (c,d) W with 0.2% glucose and 0% CaSO₄ (Mix 17) at 0, 20 and 72 h of hydration.
Figure 2.10: (a) Normalized heat; (b) Normalized heat flow of G with 0.2% glucose and 4% CaSO$_4$ (Mix 6), G with 0.2% glucose and 6% CaSO$_4$ (Mix 9) and W with 0.2% glucose and 4% CaSO$_4$ (Mix 19); (c) Normalized heat and (d) Normalized heat flow of G with 0.2% glucose and 2.5% CaSO$_4$ (Mix 8), G with 0.2% glucose and 7% CaSO$_4$ (Mix 10), and W with 0.2% glucose and 2.5% CaSO$_4$ (Mix 21).

When the CaSO$_4$ was reduced in W to 4% (Mix 18), the main reactions of C$_3$S and C$_3$A were accelerated because of the reduced CaSO$_4$ amount, and the amount of CaSO$_4$ present started to be quickly consumed by C$_3$A. Therefore, the third reaction peak that normally occurs at 18 h after CaSO$_4$ is depleted, occurred at 10 h. Similar results were reported on pure C$_3$A using various amounts of CaSO$_4$ (Pourchet et al., 2009). Furthermore, while W with 5% CaSO$_4$ and glucose (Mix 16) was retarded until 43 h (Figure 2.6), W with 4% CaSO$_4$ and glucose (Mix 19) was only retarded until 20 h (Figure 2.10). Because of the incorporation of glucose in the reaction products of C$_3$A, less glucose was available to retard C$_3$S.

In the presence of glucose, the hydration of C$_3$A can continue to a greater extent before a sufficient amount of calcium sulfoaluminate hydrates are produced to cause retardation. Afterwards, a rapid heat development occurs, exceeding the heat of Mix 16. The second C$_3$A reaction peak of Mix 19 was reduced and postponed. The delayed transition of calcium sulfoaluminate hydrates to calcium aluminate monosulfate is attributed to organic molecules entering the interlamellar region (Dosch, 1967) which is confirmed by Young (1970). The reduced peak height indicates that the amount of calcium sulfoaluminate hydrates is reduced, which is able to react with C$_3$A. The positive reaction mechanism to reduce the influence of glucose was also observed by the SEM analysis (Section 2.3.5) and in accordance with the high heat liberation in time. Additional tests using FTIR presented in Figure 2.11 indicate the presence of CSH gel at about 950 cm$^{-1}$ (Horgnies et al., 2013) for both W and G samples, with adjusted CaSO$_4$ content in the presence of glucose, while no CSH gel was observed for G with glucose until 72 h. The higher peaks in the W samples compared to G testified a higher amount of CSH gel.
Figure 2.11: FTIR spectra of: (a) G with 5% CaSO₄ (Mix 1), G with 0.2% glucose and 5% CaSO₄ (Mix 3), G with 0.2% glucose and 7% CaSO₄ (Mix 10); (b) W with 5% CaSO₄ (Mix 14), W with 0.2% glucose and 5% CaSO₄ (Mix 16) and W with 0.2% glucose and 4% CaSO₄ (Mix 19).

In the case of W with 2.5% CaSO₄ (Mix 20), a similar trend was observed when compared to Mix 18 with 4% CaSO₄. However, in the case of W with 2.5% CaSO₄ and glucose (Mix 21), a high initial heat release of 52 J/g was observed (at 30 min), which is 20% more as compared to Mix 17 with 0% CaSO₄ and glucose. The retardation was reduced to a similar extent, compared to Mix 19 having 4% CaSO₄ and glucose (increased heat release around 20 h), but the total heat release was exceeded. Furthermore, the lower formation of calcium sulfoaluminate hydrates, which is affected by glucose together with a higher percentage of C₃A dissolved, resulted in the absence of the formation of calcium aluminate monosulfate hydrates.

Ramachandran (1996) found that the incorporation of acids into the first formed structures of the metastable hexagonal, calcium aluminate, and ferrite hydrates occur. It is assumed that metastable hexagonal phases C₄AH₆ from C₃A (Milestone, 1977) and C₄FH₆ from C₄AF are influenced. As a consequence, stable and impermeable sheets of hexagonal hydrates are formed around the cement compounds and prevent the further access of water (Ramachandran, 1996). This is in line with the present findings. In addition, the findings presented in this paper for G and W allow for a distinction between reaction products formed by C₃A and C₄AF hydration since C₄AF was absent in W. The reduction of CaSO₄ in G lead to an increased retardation by the increased formation of calcium aluminate ferrite hydrates (Cuesta et al., 2015) derived from the reaction of C₄AF (Figure 2.12). This, while increasing the CaSO₄, lead to an increment of calcium sulfoaluminoferrite phases (Cuesta et al., 2015) that allowed the continuous reaction of the cement. For W, a reduction inCaSO₄ lead to an increased production of calcium aluminate phases (Figure 2.12), which in turn allowed the further reaction of cement due to their different stacking. However, by increasing the CaSO₄ significant amount of calcium sulfoaluminate, phases are formed that retard the further reaction of the cement. Therefore, the chemical composition of cement determines which phases are prominent, and in the presence of glucose, this can suppress the retardation effect.
Figure 2.12: Reaction mechanism in the presence of glucose forming permeable and impermeable layers of hydration products.

2.3.4 Effect of glucose content

In case of a higher glucose content e.g. glucose/(C₃A+C₄AF) mass ratio of 1.76\% for G and 2.72\% for W, as presented in Figure 2.13, the retarding effect for G with 5, 4, and 6\% CaSO₄ (Mix 11 - 13) increased, and the same applies to W types with 4 and 5\% CaSO₄ (Mix 22, Mix 23).

For G, a greater glucose content lead to a similar dissolution peak of 50 J/g at 10 h (Mix 3 and Mix 11). However, when the CaSO₄ content was adjusted to 6\%, the initial dissolution was increased from 50 J/g to 80 J/g (Mix 6 and Mix 13). Furthermore, the retarding effect on Mix 13 was observed up to 45 h, while with a glucose/(C₃A+C₄AF) ratio of 1.17\% (Mix 8) it was 18 h. This indicates that an increase of the glucose content by 50\% doubles the retardation effect. For W, the dissolution peak of Mix 22 was slightly higher (25 J/g) compared to that of Mix 16 (20 J/g) having a glucose/(C₃A+C₄AF) ratio of 1.76\%. The higher glucose content of Mix 22 resulted in retardation until 68 h and 50
h for Mix 16 with the same level of heat. With an adjusted CaSO$_4$ content of 4% (Mix 23), a heat release of 90 J/g at 10 h was obtained, which is significantly higher compared to a lower glucose amount (Mix 19). With an increased glucose content and adjusted CaSO$_4$ content, the initial heat release increased, indicating a higher dissolution and more glucose forms, acids, and complexations with the C$_3$A products.

Collepardi et al. (1984) found that in the presence of portlandite with 0.1% glucose, the formation of ettringite only occurred in the first 3 days and was within 7 days transferred to monosulfate. However, in the presence of portlandite and 0.3% glucose, a remarkable retarding effect on the ettringite production and gypsum consumption occurred, and no monosulfate was present at 7 days. According to Milestone (1977), the cement hydration can only continue when either the sheets are broken down when the organic molecules would be degraded by the alkalis or when no sugars are present to maintain the interlayered complex. However, the formation and later breaking down of an impervious coating of interlayered organic hexagonal hydrate complexes (as previously described) still needs further investigation.

Comparing the reaction of G with 6% CaSO$_4$ (Mix 13) and W with 4% CaSO$_4$ (Mix 23), G showed a retardation after the initial dissolution until 45 h, and then the heat release increased significantly, indicating the end of the glucose influence. However, W showed a slow reaction after the initial dissolution and the glucose influence remained prominent for more than 90 hours. This shows that both systems react differently, attributed to the presence/absence of ferrite phases. The amount of glucose seemed to change the reaction of W since a continuous liberation of heat was not observed with lower glucose concentrations or when using grey cement.

2.3.5 Mechanical properties of mortars and wood-cement composites

From the strength results presented in Figure 2.14, it is clear that initially the strength development was reduced for all glucose systems compared to the samples without glucose. The results show that G (Mix 1) compared to W (Mix 14) had a higher early strength development. This was not expected as W has a higher C$_3$S content. However, a higher porosity was found, caused by the poor workability of W series leading to air enclosure. After 7 days, the strength development of all W variants with glucose (Mix 17 and 19) exceeded the strength of the mixture containing W without glucose. In the same period, the G with glucose variants (Mix 3, Mix 10) also started to develop strength. Mix 3 shows a significantly slow strength development up to 3 days (with a compressive strength of ~1MPa), while Mix 10 at 3 days already had a strength of 10 MPa. However, at 28 days Mix 3 exceeded the reference sample, with a strength increase of about 21%. The lower initial reaction but better ion distribution (homogeneous nucleation) lead to a high surface area CSH, refining the microstructure of the hydrated cement at a later age (Lieber and Richartz, 1972; Garci Juenger and Jennings, 2002).
Figure 2.14: (a) Flexural strength; (b) Compressive strength of mortars G with 5% CaSO\(_4\) (Mix 1), G with 0.2% glucose and 5% CaSO\(_4\) (Mix 3), G with 0.2% glucose and 7% CaSO\(_4\) (Mix 10), W with 5% CaSO\(_4\) (Mix 14), W with 0.2% glucose and 5% CaSO\(_4\) (Mix 16) and W with 0.2% glucose and 4% CaSO\(_4\) (Mix 19).

The higher dosage of 7% CaSO\(_4\) in G (Mix 10) lead to an increased reaction of C\(_3\)A and C\(_4\)AF, which incorporated glucose and reduced the retardation of other cement components, having a higher strength performance than the mixture with 5% CaSO\(_4\) (Mix 3). The use of 4% CaSO\(_4\) in W (Mix 16) indeed lead to an increase in the early strength development (i.e., resulting a compressive strength of 4 MPa after 24 h and 24 MPa after 48 h). An increased amount of reaction products was also observed from the SEM pictures of the mortars with G having 5% and 4% CaSO\(_4\) in the presence of glucose (Mix 3 and Mix 6) and W having 5% and 4% CaSO\(_4\) in the presence of glucose (Mix 16 and Mix 19), as presented in Figure 2.15. The SEM analyses confirmed the hydration retardation on the G variants, indicated by a higher amount of unreacted particles and lower gel formation compared to W with an adjusted CaSO\(_4\) content.

Comparing the mechanical properties with the hydration heat release results, it is evident that the heat release varied per cement type, depending on the chemical phases present. Therefore, caution is required when a comparison is made with heat release data from different researchers using various cement types. The comparison can only be made when using the same cement types since the reaction mechanism of cement will be altered, yielding a change in the liberation of heat.
Chapter 2

Figure 2.15: SEM analysis of: (a) G with 0.2% glucose and 5% CaSO₄ (Mix 3); (b) W with 0.2% glucose and 5% CaSO₄ (Mix 16); (c) G with 0.2% glucose and 4% CaSO₄ (Mix 6); (d) W with 0.2% glucose and 4% CaSO₄ (Mix 19).

The produced WWC was dimensionally stable after 24 h of compression, indicating an appropriate hardening process. The results of the produced boards and some commercial boards with comparable densities are presented in Table 2.4. It can be seen that all produced boards showed higher or similar strength compared to the commercial WWC (termed C_WWC), indicating the validity of the binder composition proposed in this research.

Table 2.4: Evaluated WWC with their density and flexural strength properties.

<table>
<thead>
<tr>
<th>Boards*</th>
<th>CaSO₄ (wt. % cement)</th>
<th>Wood/water [-]</th>
<th>Wood/powder [-]</th>
<th>Density [kg/m³]</th>
<th>Flexural strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_WWC</td>
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<td>0.75</td>
<td>1.0</td>
<td>399.1</td>
<td>1.9</td>
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<tr>
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<td>1.0</td>
<td>455.7</td>
<td>3.0</td>
</tr>
<tr>
<td>C_WWC</td>
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<td>0.75</td>
<td>1.0</td>
<td>570.5</td>
<td>4.9</td>
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<td>1.0</td>
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<td>6.5</td>
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<tr>
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<td>0.75</td>
<td>1.0</td>
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<td>0.75</td>
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<td>528.8</td>
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</tr>
<tr>
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<td>0.75</td>
<td>1.0</td>
<td>401.3</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*All mixtures represent the recipes in Table 3 with the exception of the addition of glucose.

The boards made with G and 6% CaSO₄ (Mix 10) showed strengths exceeding the reference with pure G (Mix 1). The same applies to W having 4% CaSO₄ (Mix 19).
compared to the pure \( W \) (Mix 14), indicating the positive influence of the \( C_3A \) reaction by reducing the inhibitory effect caused by the wood. This is of high importance for this type of composite, since sufficient strength needs to be realised in an early age, as discussed in Section 2.2.1. Although the heat release presented in Figure 2.10d shows positive effects with \( W \) having 2.5\% \( \text{CaSO}_4 \) (Mix 8), the boards made with this mix design did not meet the stated requirements of the flexural strength. The reason lies in a too fast hardening of the cement layer, confirming the initial high dissolution heat in Figure 2.10d. This caused a lack of interconnection between the wood wool and a lower interaction with the soluble extractives from the wood wool.

### 2.4 Conclusions

In this chapter, the hydration kinetics of cements is studied, and the retardation of sugars on two different cements with varying \( \text{CaSO}_4 \) contents is evaluated. The retardation mechanism is studied by using isothermal calorimetry, thermal analysis, XRD, FTIR, and SEM. The findings are validated by mortars and wood wool cement composites. Based on the obtained results, the following conclusions can be drawn:

- Glucose significantly retards the hydration of both white and grey cements. Although the reduction of hydration heat release at early age is less significant in the case of grey cement due to the reaction of \( C_4AF \), the compressive strength of mortars made with white cement is much greater.
- The dosage of \( \text{CaSO}_4 \) plays a very sensitive role on the hydration of cement containing glucose. For grey Portland cement, a slight reduction of \( \text{CaSO}_4 \) content to 4\% already causes a flash set and a dramatic retardation. However, an increase of the \( \text{CaSO}_4 \) content to 7\% leads to an increased heat release and compressive strength. For Portland white cement, the reduction of \( \text{CaSO}_4 \) to 4\% results in an increased heat release and compressive strength.
- Increasing the glucose content further retards the hydration of both cement types. The retardation can be overcome by adjusting the \( \text{CaSO}_4 \) content.
- Mortars and wood wool cement composites using white cement with a reduced \( \text{CaSO}_4 \) content (4\%) and using grey cement with an increased \( \text{CaSO}_4 \) content (7\%) show reduced retarding effects and enhanced strength.

In a cement system containing glucose, the production of calcium aluminate hydrates (permeable layer) contributes to a reduced retardation, while calcium aluminate ferrite hydrates (impermeable layer) causes retardation. Furthermore, calcium sulfoaluminate hydrates (impermeable layer) cause retardation, while calcium sulfoaluminoferrite hydrates (permeable layer) do not.
Chapter 3

Design of alternative binders in wood composites


3.1 Introduction

To increase the sustainability of wood wool cement boards in terms of its CO₂ footprint, cement can be replaced by cementitious supplementary material like fly ash (FA), ground granulated blast furnace slag (GGBFS) and materials alike. The success of supplementary materials to replace cement in the concrete industry is reported extensively. However, specifically the use of calcined paper sludge fly ash as supplementary material is studied less extensively. This due to its high water demand caused by the high microporous structure, which increases the surface area, and speculated high free lime content (Bai et al., 2003; Mozaffari et al., 2009). This reduces the mechanical properties of mortars at higher replacement levels by problematic expansion (Bai et al., 2003; Mozaffari et al., 2009). Nevertheless, the superior characteristics of PsFA concerning its pozzolanic reactivity, low density compared to cement, and the negative CO₂ footprint, i.e. life-cycle analyses present a global warming equivalent of -120 kg CO₂/ton cement (Ewijk, 2008; Keulen, 2008). The latter is because PsFA is a by-product from the incineration of waste paper for energy production and its CO₂ emission is attributable to the energy production process. Hypothetically, PsFA used as an active filler for substitution of cement in this application is suitable since (a) the low density and porous nature of PsFA can be beneficial to increase the thermal insulation and sound absorption properties by creating a lightweight WWCB with a refined microstructure; (b) aesthetic and environmental reasons, since often white Portland cement is applied to obtain a white natural appearance which nevertheless has a high carbon footprint. Since PsFA is white in colour, substitution of the white cement is suitable and will create a more sustainable product. Moreover, recent developments point towards the substitution of cement by limestone powder, although the replacement is limited since the limestone only works as an inert filler while PsFA can be characterized as an active filler providing additional reaction products; (c) increased early strength development by the presence of metakaolin and portlandite (Joshi and Lohtia, 1997; Doudart de la Grée, 2012; Subas and Emirog, 2015).

A preliminary study revealed that the substitution of cement in WWCB by >10% of PsFA leads to insufficient hardening of the binder caused by the high water demand of both the PsFA and the wood wool. Therefore, in the first part of this chapter, two treatment pathways are evaluated to increase the usability of industrially calcined PsFA by reducing its water demand. The first treatment is done by pre-wetting the PsFA with water vapour to turn the free lime into portlandite. Moreover, a further decrease in water
absorption is expected due to the modification of the surface area and micropore structure by the treatment. The second treatment method is a thermal treatment, to turn all the calcium into free lime and then pre-wet it with water vapour. The PsFA, both treated and untreated, are physically and chemically characterized. By monitoring the heat release, the reactivity of the binder is examined. The suitability of PsFA as a cement substitution is then evaluated, in wood wool composites in order to lower the environmental footprint and improve their main properties such as thermal insulation and sound absorption.

In the second section of this chapter, a binder is designed with not a porous matrix but a matrix with lower amount of voids optimizing the theoretical particle packing density of the binder. For the improvement of the packing density (Figure 3.1), the so called modified Andreasen and Andersen model is used. The model uses the particle size distribution of different powders and combines them to obtain a single powder that has an optimum packing density. First the usefulness of the model is studied by optimizing the packing density of white cement using different types of limestone powder. Afterwards, a selection is made of different powders to create a ecofriendly binder with only 30% cement with the aim to create high mechanical properties.

![Figure 3.1: Schematic representation of (a) High packing density of grains; (b) Low packing density of grains with small particles located into the surface of the porous wood structure.](image)

**3.2 Materials and methods**

The studied paper sludge fly ash originates from paper sludge, a residue from the paper recycling process consisting of very short and brittle fibers, inorganic materials and ink which cannot be used further for proper paper production. The paper sludge residue from the paper recycling process consists of 50% water, 25% cellulose fibers to strengthen the paper and 25% minerals like calcium oxide and kaolin clay to make the paper smooth. A number of studies have been performed in order to reuse the paper sludge in clay bricks (Cusidó et al., 2015) or other industrial applications (Frías et al., 2015). Nonetheless, still a large proportion of paper sludge is directly disposed at landfill sites A more favorable processing route is the incineration of paper sludge, which reduces the waste volume and in the meantime produces energy in special power plants or bio energy power plants (Doudart de la Grée et al., 2016). Moreover, the produced paper sludge fly ash (PsFA) can be applied as a substitute for soil stabilization under roads and as a supplementary cementitious material. The suitability depends on the mineralogical composition of the PsFA and the applied combustion temperature. Often on industrial scale, temperatures between 850 and 1200 °C are used, leading to a material with hydraulic properties (Ferrándiz-Mas et al., 2014). Corinaldesi et al. (2011) observed a slight increase in
compressive strength in mortar when 5 and 10% by mass of cement was replaced with PsFA. Research has shown that calcining paper sludge at 700-750 °C produces a reactive pozzolanic PsFA by forming metakaolin (Pera and Amrouz, 1998; Bai et al., 2003; Banfill and Frias, 2007; Segui et al., 2012; Giménez et al., 2014). García et al., (2008) reported an increase in the early strength of mortars produced by replacing 10% by mass of cement. Characteristics of the PsFA such as the pozzolanic activity and resulting products are well known (Frías et al., 2013, 2008; Goñi et al., 2012; Vigil de la Villa et al., 2007). However, the origin of the high water demand (Goñi et al., 2012; Wong et al., 2015; Wu et al., 2016) is studied less extensively and it seems that it is caused by the high microporous structure, which increases the surface area, and speculated high free lime content (Bai et al., 2003; Mozaffari et al., 2009). This reduces the mechanical properties of mortars at higher replacement levels by problematic expansion (Bai et al., 2003; Mozaffari et al., 2009).

Nevertheless, the PsFA characteristics make it of interest to use as a binder substitution to design a lightweight wood wool composite board (WWCB) with a refined microporous structure. Meanwhile wood is available worldwide in large quantities and its lightweight porous structure makes it of value as a filler, providing thermal and sound absorbing properties (Badejo, 1988; Jorge et al., 2004; Lee, 1985). While the binding agent cement mineralizes the wood, adding high resistance to bio-degradation (Pereira et al., 2006) and fire resistant properties (Wei et al., 2000a; Doudart de la Grée et al., 2014; Simatupang and Geimer, 1990). The production process of commercial WWCB involves firstly the mixing of wood wool and cement, then a pressing procedure for 24 h and finally a curing period of 10 days, followed by the removal of the remaining free water (Doudart de la Grée et al., 2014). Therefore, applying a binder with a fast early strength development property is desirable, i.e. the main strength development needs to be achieved within 24 h of pressing otherwise the boards will be dimensionally unstable and will gain insufficient mechanical properties. Although WWCBs have been produced since 1920 (van Elten, 2006) and used in the building environment for multiple applications like roofing of garage boxes, acoustic ceiling in non-residential buildings or in residential housing as complete wall elements the used binder still primarily consists of Portland cement leading to a high CO₂ footprint. Because of the above mentioned requirements, replacement of cement is not straightforward. Besides, under the alkaline condition of cement slurry, soluble extractives from the wood will be leached out, which withdraw water from the cement slurry and interact with Ca⁺ ions released from cement (Doudart de la Grée et al., 2017), resulting in the retardation of cement hydration.

Hypothetically, PsFA, white in color, as an active filler for substitution of cement in WWCB is suitable, since (a) the low density and porous nature of PsFA can be beneficial to increase the thermal insulation and sound absorption properties; (b) aesthetic and environmental reasons, as often white Portland cement is applied to obtain a nice appearance which nevertheless has a high carbon footprint; (c) fast early strength development is achievable, attributed to the presence of metakaolin and portlandite (Joshi and Lohtia, 1997; Doudart de la Grée, 2012; Subas and Emirog, 2015).

The treatment of PsFA resulted in the following samples: (a) pre-wetted, termed PsFA-w; (b) thermally at 750 °C, termed PSFA-h and (c) the thermal treated sample and then pre-
wetted, termed PsFA h/w (Doudart de la Grée, 2012). The amount of water to initiate the chemical upgrading of PsFA is determined based on the conversion of free lime to Portlandite.

This water dosage would be a minimum quantity since it only takes into account the transition of free lime to Portlandite while it is reasonable to expect that simultaneously other phases will also react. Furthermore, part of the water will be physically absorbed on the surface of the powder (Yu and Brouwers, 2011a). The water demand of powders is evaluated by using the Puntke test (Hunger and Brouwers, 2009). The test is performed by adding water to 50 g of powder and then stirred. The water is continuously added and the amount is measured until a shiny surface is obtained that indicates that the system reaches a saturation. Using this method also the packing density of the binder can be determined:

\[
P = \frac{V_p}{V_p + V_w} = \frac{m_p}{m_w \times \rho_p + m_p}
\]

where \( P \) is the packing of a material in the range of 0-1, with 1 is solid perfectly packed and 0 no packing; \( V_p \) is the volume of the powder [cm\(^3\)]; \( V_w \) is the volume of water [cm\(^3\)]; \( m_w \) is the mass of the applied water [g]; \( m_p \) the mass of the measured powder [g], \( \rho_p \) is the density of the powder [g/cm\(^3\)] and \( \rho_w \) is the density of water [g/cm\(^3\)]. The packing of a material provides the insight about the binder where a higher packing value leads to a denser matrix.

### 3.2.1 Characterisation of the powders

#### Physical properties

The physical properties such as the specific surface area (BET), the specific densities and the particle size distribution are measured by \( N_2 \) adsorption using a Micrometrics Tristar II 3020, an AccuPyc 1340 II gas Pycnometer and a Malvern Mastersizer 2000, respectively. The bulk density is determined by using the mass of the powder divided by the filled cup with a known volume.

#### Chemical properties

The chemical composition of the powdered samples is analyzed using an X-ray fluorescence (XRF) using an EDX Panalytical Epsilon 3X. In the case of PsFA, all calcium based compounds are considered by XRF, although they differentiate in their chemical nature such as free lime (CaO), Portlandite (Ca(OH)\(_2\)) calcite (CaCO\(_3\)), and other amorphous Ca-containing phases. Thermogravimetry (TG) analysis, (Netzsch STA F1) is performed to determine the free lime amount. The original and treated samples were heated with 10 \( ^\circ \text{C}/\text{min} \) up to 1000 \( ^\circ \text{C} \) in order to assess the content of Ca(OH)\(_2\) and CaCO\(_3\), from the mass loss caused by the removal of H\(_2\)O and CO\(_2\), respectively. Three main mass loss intervals are expected: the loss of physical water under 120 \( ^\circ \text{C} \) (Arlacon Ruiz et al., 2005; Castellote et al., 2004), the decomposition of Ca(OH)\(_2\) between 350 and 600 \( ^\circ \text{C} \) (Shui et al., 2008; Alonso and Fernandez, 2004) and the decomposition of CaCO\(_3\)
between 600 and 900 °C (Shui et al., 2008). Based on this, the effect of the treatment can be identified by observing the increase in Ca(OH)$_2$. X-ray diffraction analysis is performed using a Rigaku-Geigerflex spectrometer using Cu-K$_α$ radiation and a 2θ angle between 15 and 55º with a step size of 0.02º and 1-second count time to evaluate the effect of the treatments. The pattern processing was done using EVA software (Bruker) and the ICDD pattern database.

**Hydration kinetics**

The hydration kinetics of PsFA-w is examined by using a TAM AIR isothermal calorimeter. The tests were performed for 70 h with a water to powder ratio of 0.5 under a fixed temperature of 20 °C. The powder samples were first transferred in an ampoule and then well mixed before water was added. After the addition of water, the mixture was mixed for 2 min and the ampoule was loaded to the isothermal calorimeter. The mixtures consisting of 36% LP with 64% W (reference binder) are compared to the mixture consisting of 36% PsFA-w with 64% W, to evaluate the nucleation and seeding effects that are reflected by an accelerated hydration rate.

### 3.2.2 Mechanical properties

To investigate the suitability of PsFA as a cement replacer in wood wool composites, boards are produced by applying the mixture PsFA-w and CEM I 52.5 R White (termed W) according to the method proposed in a previous study (Doudart de la Grée et al., 2017). The target density of the board is 450 kg/m$^3$ using a water-to-powder ratio by mass of 1.0 and a wood-to-powder ratio by mass of 0.75. The recipes are presented in Table 3.1. The substitution level of the reference binder (64% W +36% LP termed B1) by 10 and 20% is evaluated, termed B2 and B3 respectively. Moreover, substitution of cement (no LP) by PsFA-w using 36% and 60% as an active filler is investigated, termed B4 and B5 (see Table 3.1).

Firstly, the wood is pre-wetted with water, corresponding to 30% of the dry mass of wood wool, to make the wood wool more flexible and less vulnerable to break. Secondly, the binder is mixed with water for 1 min to create a homogenous slurry, which is then applied on the wood wool and then mixed for approximately 30 s. Thirdly, the wood wool cement composite is transferred to a mold with a size of 30 × 50 cm$^2$ (W × L). Fourthly, the mold is removed and the composite is compressed to the desired height that is determined by using distant holders of 15 mm for 24 h, followed by an ambient curing for 10 days. Finally, the boards are dried in an oven at 60 °C for 22 h to remove the capillary water, and three samples of 15 × 20 cm$^2$(W × L) were extracted. The apparent density of the boards was determined by the measured mass and bulk volume. The flexural strength was measured using a three point flexural testing instrument in accordance with EN 12089.
Table 3.1: Mix proportions of the tested mixtures, W/B is the wood to binder ratio and W/P is the water to powder ratio. With W standing for CEM I 52.5 R White, LP for limestone powder and PsFA-w for water treated papersludge fly ash.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composite recipes</th>
<th>W [%]</th>
<th>LP [%]</th>
<th>PsFA-w [%]</th>
<th>W/B</th>
<th>W/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0.64 W + 0.36 LP</td>
<td>64</td>
<td>36</td>
<td>0</td>
<td>0.75</td>
<td>1.0</td>
</tr>
<tr>
<td>B2</td>
<td>0.57 W + 0.33 LP + 0.1 PsFA-w</td>
<td>57</td>
<td>33</td>
<td>10</td>
<td>0.75</td>
<td>1.0</td>
</tr>
<tr>
<td>B3</td>
<td>0.51 W + 0.29 LP + 0.2 PsFA-w</td>
<td>51</td>
<td>29</td>
<td>20</td>
<td>0.75</td>
<td>1.0</td>
</tr>
<tr>
<td>B4</td>
<td>0.64 W + 0.36 PsFA-w</td>
<td>64</td>
<td>0</td>
<td>36</td>
<td>0.75</td>
<td>1.0</td>
</tr>
<tr>
<td>B5</td>
<td>0.4 W + 0.6 PsFA-w</td>
<td>40</td>
<td>0</td>
<td>60</td>
<td>0.75</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3.2.3 Thermal insulating properties

Fly ash and biomass ashes have shown a positive contribution to lower the thermal conductivity (Jafari and Jung, 2016). The effect of the PsFA-w on the thermal properties of the WWCB was evaluated by determining the thermal conductivity and porosity of the produced boards. The thermal conductivity was measured using a commercial heat transfer analyzer (ISOMET 2104, Applied Precision). The porosity of the board was measured using a AccuPyc 1340 II gas Pycnometer. Besides, the morphological properties were studied by scanning electron microscopy (SEM) analysis.

3.2.4 Sound absorbing properties

Since sound absorption is one of the main features of wood wool composite boards, the influence of PsFA on the sound absorbing properties of the boards was investigated. The sound absorption properties of a wood wool composite using the reference binder with a thickness of 15 mm (B1) were measured and compared with a 15 mm sample by replacing the same recipe by 20% PsFA-w (B3). The sound absorption was calculated using a “slit pore model” by measuring the impedance using an impedance tube. The reason that only 20% PsFA-w is studied is due to the required sample size and limitations of the measurement set-up. The composite with a very low density turns brittle and can be possibly broken by the cylindrical cutting force for preparing the sample with a size of 40 mm in diameter for the acoustical test. It needs to be noted that this data cannot be compared to the EN ISO 354 reverberation room test since it does not take into account a diffuse field. Nevertheless, it provides a fair comparison between the sound absorption of the different mixtures and it can be used as a primary indicator for the sound absorbing properties of the boards.

3.2.5 Thermal analysis

The mineralization of wood wool by the binder leads to an improved fire resistance by reducing the combustibility of the wood wool. However, the fire behavior of the composites is altered when different mineral compositions are applied. Therefore, TG tests were performed after the boards were cured and dried to estimate the rate of wood wool combustion. The mass loss was measured using a heat rate of 10 °C/min to a temperature of 620 °C for wood at which cellulose, hemicellulose and lignin will decompose (Drysdale, 2011) and 1000 °C for the hydrated binders. The total mass loss of the composites up to 620 °C is attributed to the combusted wood wool and dehydrated binder. Hence, the inherent percentage mass loss of binder was measured and normalized to the amount of binder present in the composite. This quantity was subtracted from the mass loss of WWCB and the difference was accounted for the mass loss of wood.
3.3 Results and discussions

3.3.1 Characteristics of the binders

PsFA has a BET surface area of 8.20 m$^2$/g (see Table 3.2). The high surface area and the presence of a high amount of micropore area (1.34 m$^2$/g) and cumulative volume of pores (0.03 cm$^3$/g) testify its porous microstructure. Figure 3.2 presents the particle size distribution and cumulative volume of the materials illustrating that PsFA is coarser compared to the other materials. The specific density ($\rho_s$) of PsFA is in the range of cement, however, the loosely packed bulk density ($\rho_b$) is very low, more than a factor of two lower (490 kg/m$^3$) compared to that of cement (1100 kg/m$^3$), confirming again the high porosity.

Table 3.2. Cumulative volume; specific surface areas; specific density ($\rho_s$) and bulk densities ($\rho_b$) and the mean particle size distribution of the powders used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cumulative volume of pores [cm$^3$/g]</th>
<th>T-plot micropore area [m$^2$/g]</th>
<th>BET surface area [m$^2$/g]</th>
<th>$\rho_s$ [kg/m$^3$]</th>
<th>$\rho_b$ [kg/m$^3$]</th>
<th>D$_{50}$ [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PsFA</td>
<td>0.030</td>
<td>1.34</td>
<td>8.20</td>
<td>2850</td>
<td>490</td>
<td>30</td>
</tr>
<tr>
<td>W</td>
<td>0.004</td>
<td>-</td>
<td>1.21</td>
<td>3150</td>
<td>1090</td>
<td>17</td>
</tr>
<tr>
<td>LP</td>
<td>0.005</td>
<td>0.28</td>
<td>1.24</td>
<td>2700</td>
<td>1000</td>
<td>10</td>
</tr>
</tbody>
</table>

Figure 3.2: Particle size distribution: (a) Fraction volume; (b) Cumulative volume.

From Table 3.3 it is evident that PsFA has a high calcium content, resulted from the filler used for paper making. The moderate silica and aluminum contents are from the calcining of the kaolin clay used for paper making (Pera and Amrouz, 1998; Bai et al., 2003; Banfill and Frias, 2007; Segui et al., 2012).
Table 3.3: Oxide composition determined by XRF after subtraction of the LOI.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>PsFA [%]</th>
<th>W [%]</th>
<th>LP [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>49.0</td>
<td>67.2</td>
<td>89.6</td>
</tr>
<tr>
<td>SiO₂</td>
<td>19.7</td>
<td>20.9</td>
<td>4.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.7</td>
<td>3.9</td>
<td>1.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.0</td>
<td>0.5</td>
<td>1.6</td>
</tr>
<tr>
<td>MgO</td>
<td>2.4</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Other Oxides*</td>
<td>17.2</td>
<td>7.1</td>
<td>2.4</td>
</tr>
</tbody>
</table>

*Oxides lower than < 0.5%

As can be seen in Table 3.4, PsFA shows a higher water demand of 69% of the dry mass compared to 26.4% for W and 21.6% for LP. The packing fraction of the PsFA due to the high water demand is significantly low, indicating that especially at higher replacement levels the mechanical properties could be strongly affected because of the reduced densification of the matrix. Moreover, it should be noted that the temperature of PsFA started to increase after the addition of certain amount of water, attributed to the fast hydration of free lime that would lead to thermal cracks and expansion (Bai et al., 2003; Mozaffari et al., 2009).

Table 3.4: Packing of materials using the Puntke test eq. (3.1). Water demand is measured for 50 g of material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Water demand [g]</th>
<th>Packing</th>
</tr>
</thead>
<tbody>
<tr>
<td>PsFA</td>
<td>34.6</td>
<td>0.34</td>
</tr>
<tr>
<td>W</td>
<td>13.2</td>
<td>0.55</td>
</tr>
<tr>
<td>LP</td>
<td>10.8</td>
<td>0.63</td>
</tr>
</tbody>
</table>

The mass losses to determine the stoichiometrically calculated amounts of Ca(OH)₂ and CaCO₃ are presented in Table 3.5. 2.47% of Ca(OH)₂, 37.18% of CaCO₃ and 26.30% of Ca-containing phases are found for PsFA. PsFA-h shows that a low amount of water (2.30%) is still present after the thermal treatment, representing the rehydration of the free lime while almost all CaCO₃ is turned into CaO and the remaining 0.39% is possibly resulted from the carbonation of Ca(OH)₂, both occurred during the storage. Based on the remaining CaO amount of 26.30% for PsFA and 47.04% for PsFA-h, the minimum required water amount is estimated for the transition to portlandite, indicating that 8.4% and 15.1% of water is needed, which would be valid if all CaO is free lime.

Table 3.5: Mass loss of original and treated PsFA and predicted % of Ca-containing compounds.

<table>
<thead>
<tr>
<th></th>
<th>PsFA [%]</th>
<th>PsFA-h [%]</th>
<th>PsFA-w [%]</th>
<th>PsFA-h/w [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-150°C</td>
<td>0.14</td>
<td>0.05</td>
<td>1.72</td>
<td>1.53</td>
</tr>
<tr>
<td>350-600°C</td>
<td>0.6</td>
<td>0.56</td>
<td>2.71</td>
<td>9.08</td>
</tr>
<tr>
<td>600-900°C</td>
<td>16.35</td>
<td>0.17</td>
<td>14.07</td>
<td>0.93</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>2.47</td>
<td>2.30</td>
<td>11.15</td>
<td>37.34</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>37.18</td>
<td>0.39</td>
<td>32.00</td>
<td>2.12</td>
</tr>
<tr>
<td>CaO*</td>
<td>22.70</td>
<td>1.96</td>
<td>26.36</td>
<td>29.45</td>
</tr>
<tr>
<td>CaO**</td>
<td>26.30</td>
<td>47.04</td>
<td>22.64</td>
<td>19.55</td>
</tr>
</tbody>
</table>

* % of CaO content from Ca(OH)₂ and CaCO₃  ** % of CaO after subtraction of the CaO in Ca(OH)₂ and CaCO₃ from the CaO obtained by XRF
Applying 8.4% of water did not lead to any noticeable formation of portlandite which can be explained by the high water demand of the powder, as shown by the Puntke test. Hence, a water treatment is chosen based on the 15.1% of possible free lime when heating the sample and an additional 10% accounting that part of the water will be surface related. Therefore, a pre-wetting of 25% of the dry mass of powder for both PsFA and PsFA-h is further evaluated for portlandite formation using TG. In the case of the PsFA-w sample (Table 3.5), the treatment led to a Ca(OH)$_2$ amount of 11.15% which is 8.68% more compared to the untreated PsFA. In the case of PsFA h/w, the conversion of free lime with the same amount of water led to a Ca(OH)$_2$ content of 37.34%, an increase of 34.88% compared to PsFA. Moreover, both results indicate that not all the CaO in PsFA-w and PsFA h/w is turned to portlandite, indicating the existence of free lime or other calcium containing phases.

A preliminary XRD analysis shows that no amorphous compounds are detectable in PsFA, while metakaolin may exist in the fine particles in the range of 0-20 µm (Tafraoui et al., 2009). Therefore, for a more representative analysis, PsFA is separated to two fractions of (1) particles smaller than 20 µm and (2) particles larger than 20 µm. The obtained XRD results are presented in Figure 3.3. It can be seen that PsFA originally consists of a high content of CaCO$_3$ and some small peaks of CaO and SiO$_2$. After the water treatment, the CaO is reduced and the formation of Ca(OH)$_2$ is detected.
Chapter 3

Figure 3.3: Highlighting the crystal Ca-containing phases: CaCO$_3$ (■), CaO (□), SiO$_2$ (◊) and Ca(OH)$_2$ (○) for (a) XRD-pattern of original (<20 mic. and >20 mic.) and thermal PsFA; (b) original, water and thermal water treated PsFA.

After the thermal treatment, almost no CaCO$_3$ or Ca(OH)$_2$ could be detected in PsFA-h and only CaO is identified. PsFA h/w shows that the CaCO$_3$ is turned into CaO and later into Ca(OH)$_2$. However, not all lime is transformed into Ca(OH)$_2$, which confirms the TG analysis. Moreover, the TG results show that compared to PsFA, the amount of Ca(OH)$_2$ in PsFA-w is increased and the XRD analysis indicates that an amount of free lime is still present after the treatment. Menéndez (2012) studied the rehydration of CaO when CaCO$_3$ decomposed at 650 and 1000°C and concluded that at 650°C, 80% of CaO could rehydrate while at 1000°C only 20-40% will rehydrate, which is in agreement with the present study. From the XRD results, no additional crystalline phases are observed after the treatments. Although additional analysis of PsFA-w indicated that by the water treatment the BET surface area was reduced to 6.91 m$^2$/g and the micropore area and pore volume to 0.91 m$^2$/g and 0.28 cm$^3$/g, suggesting that reaction of Portlandite and other amorphous phases occur that could influence the reactivity of the material.

3.3.2 Hydration kinetics

The heat release results, shown in Figure 3.4, present a fast reaction for W with a $T_{\text{max}}$ at 20 h due to the second stage reaction of C$_3$A and ettringite, forming monosulfate. Replacing W with 36% LP (binder used in B1) leads to a faster reaction, showing a $T_{\text{max}}$ at 11 h attributed to the nucleation effect of LP (Bonavetti et al., 2001). Replacing W with PsFA-w (binder used in B4), a further acceleration is visible, with the $T_{\text{max}}$ occurring at 9 h, indicating that indeed the material attributes to a fast early reaction providing similar heat compared to the use of LP while having a coarser particle size. This is possibly due to the provided extra C-S-H seeding (Thomas et al., 2009), created after the water treatment as part of the water is also used to form gel or reaction of metakaolin.
3.3.3 Mechanical properties

Figure 3.5 displays the bending strength of WWCB versus the density manufactured with the composition as described in Table 3.2. In most of the replacement levels, the material behaves similar compared to the reference sample B1, up to the replacement level of 20% (B3). At higher replacement levels, the binder matrix is found too weak since the present limestone powder insufficiently contributes to the gel formation, leading to a bending strength that could not fulfill the stated requirement of 1.7 MPa (Mencnarowski, 2014), which therefore are excluded from the results.

Figure 3.5: The bending strength versus apparent density of boards produced with the treated PsFA as 10 and 20 % replacement (B2 and B3) of the reference binder (B1). Moreover, a mixture of 36% (B4) and 60% (B5) PsFA-w as cement replacement.
The effect of PsFA-w as an “active filler” is further confirmed by the bending strength of PsFA-w when replacing cement by 36% (B4) and 60% (B5), as presented in Figure 3.5. Both samples give higher strength than B1. Thus, the potential of using PsFA-w as a cement replacement is demonstrated for wood-cement composites.

The reason for this behavior can be explained by the treatment: firstly, the pre-added water turns part of the free lime into Ca(OH)$_2$ that leads to a reduction in the surface area and water demand of the PsFA-w. Therefore, when creating a slurry consisting of PsFA-w, cement and water, more water is available for the cement hydration. While without treatment, a higher water amount would be needed, leading to an increased ion migration to the wood due to the hydroscopic nature of the wood wool (Wei et al., 2004; Pereira et al., 2005; Pereira et al., 2012). Secondly, by the reaction of metakaolin (Pavlík and Užáková, 2016) present in PsFA-w (Frías et al., 2015) the binder reacts fast as indicated by the isothermal calorimeter results. Simultaneously C$_3$A in cement reacts with water and Ca(OH)$_2$ (the latter is provided by the reaction of cement or PsFA-w), forming calcium aluminate hydrates in the form C$_2$AH$_8$ and C$_4$AH$_8$ that later turn into a more stable hydrate C$_3$AH$_6$ (Taylor, 1990). Because of this conversion, water is removed, decreasing the porosity of the binder (cement with PsFA-w). Thirdly, the low bulk volume of PsFA-w leads to a better surface coverage of the wood wool (Figure 3.6a compared to 3.6b) when applying the same mass amount as cement or limestone powder (Table 3.2). This increases the interlocking between the wood wool strands by means a higher contact area (Figure 3.6c). Furthermore, the high porosity of the boards would allow small expansion caused by the high amount of PsFA while in mortars this might lead to reduced mechanical properties. Finally, the concentration of calcium ions in cement is compensated by adding an additional source of calcium from PsFA-w. Although the interaction between Ca$^+$ ions and wood forming complexations still occurs, the inhibitory effect on the binder hydration is reduced. When the strength results of the boards in this study are compared with boards using only CEM I 52.5 R White as binder (Doudart de la Grée et al., 2017), the boards made with PsFA in a density class of 450 kg/m$^3$ are having a similar or higher bending strength depending on the replacement level.
3.3.4 Thermal properties

The thermal conductivity results of the tested samples are summarized in Table 3.6 (presented as an average of 5 samples with spread). It can be seen that the thermal conductivity of the WWCB is decreased when increasing the replacement percentage of cement by PsFA-w. The board density is reduced and the porosity is accordingly increased. The reduction in density can be explained by the microstructure of PsFA-w using SEM, as illustrated in Figure 3.7. The matrix of B4 (Figure 3.7a and b) consists of a large amount of needle-shaped particles, identified as ettringite together with hexagonal plates of Ca(OH)$_2$ and gel-like structures. During the drying of the material in the oven at 60 °C to remove the extra water, part of the chemically bound water in ettringite is also released, increasing the mass loss and reducing the density of the boards. The micro porous structure is clearly visible, compared to a denser structure of B1 (Figure 3.7c and 3.7d). The low thermal conductivity improves the thermal insulation properties allowing the implementation of this type of composite in large wall structures, which are recently developed for low cost housing.

Table 3.6: The measured physical properties of different composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composite</th>
<th>Thermal conductivity [W/(m·K)]</th>
<th>Porosity [%]</th>
<th>Density [kg/m$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>0.64 W + 0.36 LP</td>
<td>0.085 ±0.005</td>
<td>76.7</td>
<td>490</td>
</tr>
<tr>
<td>B2</td>
<td>0.57 W + 0.33 LP + 0.1 PsFA-w</td>
<td>0.083 ±0.002</td>
<td>79.5</td>
<td>389</td>
</tr>
<tr>
<td>B3</td>
<td>0.51 W + 0.29 LP + 0.2 PsFA-w</td>
<td>0.075 ±0.001</td>
<td>77.6</td>
<td>440</td>
</tr>
<tr>
<td>B4</td>
<td>0.64 W + 0.36 PsFA-w</td>
<td>0.073 ±0.002</td>
<td>76.5</td>
<td>448</td>
</tr>
<tr>
<td>B5</td>
<td>0.4 W + 0.6 PsFA-w</td>
<td>0.070 ±0.002</td>
<td>79.1</td>
<td>400</td>
</tr>
</tbody>
</table>
3.3.5 Acoustical properties

The influence of 20% PsFA-w replacement of the reference binder (B3) on the sound absorbing properties of the WWCB is presented in Figure 3.8, in the frequency range 125-2000 Hz. It needs to be noted that two different kinds of porosities can be defined, namely: (1) the measured “open porosity” by using for instance a gas Pycnometer and (2) the “acoustically effective porosity” that is defined as the porosity of a material that takes part in the acoustical process (more information can be found in Section 6.3.4). It was found that increasing the bulk density of boards leads to a decrease of the open porosity but an increase of the acoustically effective porosity (Botterman et al., 2016b). This can be explained by: (1) not all the voids in the wood binder matrix are involved in the acoustical process (Glé et al., 2012; Wassilieff, 1996) and (2) not all the voids between the binder covered wood wool strands are involved in the acoustical process (Fuchs, 2013).

Although the density of the boards using 20% PsFA is reduced, the low bulk density of PsFA leads to a similar effect as a higher density board, namely the reduction of the voids between the wood wool strands by the high volume of the porous binder.
Without PsFA, the voids between the wood wool strands are not efficiently taking part in the acoustical process. Hence, by using PsFA-w, refinement of the micro structure of the board by micropores is achieved, consequently resulting in an improvement of the sound absorption of the board e.g. two times better compared to the reference sample. This results are in line with the results of boards made without PsFA in a separate study (Figure 6.11 in Section 6.4.2).

![Graph showing sound absorption](image)

**Figure 3.8**: Sound absorption of 15 mm thickness boards using a slit pore model where the binder consists of 0.64 W + 0.36 LP (B1) as reference sample and the binder replaced with 20% PsFA-w (B3).

### 3.3.6 Performance at high temperature

Figure 3.9 indicates the mass loss of a commercial WWCB (B1), wood wool and boards made of 40% PsFA-w as cement replacement (B4), pre-heated at 100 °C and then heated to 1000 °C. The wood wool was only investigated until 620 °C since between 200-260 °C hemicellulose and between 240-350 °C cellulose are removed, respectively and lignin starts to decompose between 280-500 °C (Drysdale, 2011). Before 120 °C, wood wool loses about 9% of its mass because of the evaporation of water. At 620 °C, the majority of the wood is combusted and only 25% of the initial mass remains. The wood wool composites B1 and B4 lose at 600 °C 29% and 36% of their mass respectively. Figure 3.10 presents the mass loss of the hydrated binders without wood, indicating a loss of 21% when using B4 and 17% when using B1. It is found that 41.2% and 55.3% of the wood wool is combusted for B1 and B4 respectively, which is lower compared to the 75% mass loss without using any binder. Nevertheless, the fire resistance of a material is not only indicated by its mass loss. Like the case with gypsum boards (Yu and Brouwers 2012; Yu and Brouwers, 2011b), chemically bound water present in PsFA-w is released during heating as moisture, effectively retarding the heat transfer by a so called gas retention phenomenon (Grossel, 2003; Thomas et al., 2009). In densely packed materials (e.g. concrete), the steam causes thermal spalling since the vapors are causing expansion of matrix and increase the pressure in the voids. However, the binder matrix of WWCB has a high pressure capacity due to its high porosity by the incorporation of PsFA-w, hence vaporization of the moisture has a less effect concerning the thermal spalling. Furthermore, the formed steam migrates towards the colder regions, and becomes re-
absorbed in the neighboring layer pores. Gradually this leads to a saturated layer hindering the gas flow (moisture clogging) by forming a front between the dry and saturated layer (Chen et al., 2009; Vickers, 2015). Moreover, even after the complete dehydration, the present calcium carbonate will start to decompose which requires certain energy and the binder continues to act as a heat insulating barrier due to its high thermal mass.

**Figure 3.9:** TG curves of wood wool, reference board (B1) and 40% W replaced by PsFA-w (B4).

**Figure 3.10:** TG curves of reference (B1) and 60% C52.5 + 40% PsFA-w (B4).
3.4 Optimized mix design

3.4.1 Mix design algorithm

The used particle packing model, the so-called modified Andreasen and Andersen model, proposed by Funk and Dinger (1994) is expressed as:

\[ P(D) = \frac{D^q - D^q_{\text{min}}}{D^q_{\text{max}} - D^q_{\text{min}}} \]  

(3.2)

where \( P(D) \) is a fraction of the total solids being smaller than size \( D \), \( D \) is the particle size [μm], \( D_{\text{max}} \) is the maximum particle size [μm], \( D_{\text{min}} \) is the minimum particle size [μm], and \( q \) is the distribution modulus.

The modified Andreasen and Andersen (A&A) model was firstly applied in the design of concrete products by Brouwers and Radix, (2005). Afterwards it was also successfully used in the optimization algorithms of self-compacting concrete (Hunger, 2010), zero-slump concrete (Husken, 2010), lightweight concrete (Yu, 2011), nano-silica modified concrete (Quercia, 2014), high performance concrete (Yu, 2015) and alkali activated slag fly ash binders (Goa, 2017).

This method helps to combine materials with different particle size distributions into one “composed mix”, termed “target line”, which possess a continuous grading line. The choice of the \( D_{\text{min}} \) and \( D_{\text{max}} \) depends on the minimum and maximum grain size of the powders that are used. Using the optimization algorithm a target line was created with a \( D_{\text{max}} \) as 95% and \( D_{\text{min}} \) as 5% of the particle size distribution of G (CEM I 52.5 R). The q value is related to the type of mixture, e.g. when a smaller q value is applied, the composed mix will be rich in fine particles. For instance, in case a q value of 0.5 would be chosen, the particles below 30 micron would be reduced from 50% to 30%. In case of the wood wool cement board a q value of 0.23 is considered (Yu, 2012), since the roughness of the wood wool requires more fine particles to create a good bond at the interfacial transition zone between the external surface of the wood wool and the hydrated binder. Moreover, the curing of WWCB lasts 10 days and therefore only the small particles will react.

3.4.2 Particle size distribution

Before improving the particle packing the suitability of the model for wood wool cement boards is validated. For this G is replaced with 30% inert quartz powder, known under the commercial name Silverbond M600, M400, M300 an M10 is used ordered from fine to coarse. The created mixtures will defer in particle size and deviate from the optimum target line which represents an optimized packing. The particle size distributions of the quartz powders together with the used cement, G are presented in Figure 3.11. It is found that M600 is the finest material with a \( d(0.9) \) of 10 μm, M400 with a \( d(0.9) \) 30 μm, M300 with a \( d(0.9) \) 50 μm and M10 with a \( d(0.9) \) 70 μm.
The composed particle size distributions of powders containing 30% quartz powder and 70% cement were calculated and compared with the proposed target line. The deviation between these lines is presented in Table 3.7 and illustrated in Figure 3.12. It can be seen that the composed mix with the coarse quartz powder (M10) results in a relatively coarse mix compared to the target line. Increasing the fines will eventually (in case of M400) result in a mixture having almost identical particle size distribution as the target line. Using the finer quartz powder like M600 will result in a mixture containing more fine particles.

Figure 3.11: Particle size distributions of G (CEM I 52.5 R) and quartz powder M600, M400, M300 and M10.

Figure 3.12: Particle size distributions of target line for (a) M10 composed mix.; (b) M300 composed mix.; (c) M400; (d) M600.
3.4.3 Evaluation of an optimized mix design

Table 3.7 presents the results of the tested materials, indicating the $D_{\text{max}}$ and $D_{\text{min}}$ and the deviation between the composed mix and the target line. The deviation value is obtained by computing the surface area between the target line and composed line. The higher the deviation the larger the difference between the created composed mix and the target line. The mixture with fine M600 and coarse M10 fractions shows the lowest bending strength. For the mix with finer particles M400, the strength is higher. When comparing the particle size distributions of the different composites as illustrated in Figure 3.12, the M400 mixture corresponds best with the target line. From the obtained results, the composed mix with M400 indeed obtained the highest mechanical properties. The improved strength was caused not only by an improved packing but also by the influence of the particle size. Small particles help to create nucleation sites; however, if too many small particles are used, e.g. in case of M600, the bridging of the wood wool becomes difficult, resulting in the reduction of mechanical properties. The same applies to the very coarse particles that help to improve the bridging but result in a more porous matrix lowering the mechanical properties.

Table 3.7: Mixtures of different materials with their particle size deviation compared to the target line together with board density and bending strength.

<table>
<thead>
<tr>
<th>Material</th>
<th>Deviation [μm]</th>
<th>$D_{\text{max}}$ [μm]</th>
<th>$D_{\text{min}}$ [μm]</th>
<th>Board density [kg/m$^3$]</th>
<th>Bending strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>M600</td>
<td>577</td>
<td>60.26</td>
<td>1.1</td>
<td>410</td>
<td>3.51</td>
</tr>
<tr>
<td>M400</td>
<td>82</td>
<td>60.26</td>
<td>1.1</td>
<td>408</td>
<td>4.74</td>
</tr>
<tr>
<td>M300</td>
<td>380</td>
<td>60.26</td>
<td>1.1</td>
<td>415</td>
<td>3.67</td>
</tr>
<tr>
<td>M10</td>
<td>787</td>
<td>60.26</td>
<td>1.1</td>
<td>396</td>
<td>2.83</td>
</tr>
</tbody>
</table>

Results above show the potential use of an optimized packing algorithm and confirm the earlier stated hypothesis.

3.4.4 Validation

Based on the previous results, three additional recipes were tested: (1) with 100% CEM I 52.5 R, (2) with 30% by mass replacement by ground granulated blast furnace slag (GGBFS) and (3) with additional pozzolans and fillers with ratios according to the ideal packing algorithm, as presented in Figure 3.13. The bending strength of the produced boards is presented in Table 3.8.
Figure 3.13: Particle size distributions of G (CEM I 52.5 R), Latent hydraulic binder, two fillers together with the target line and created composed mix.

From Figure 3.13 the difference in particle size distribution of the chosen materials can be seen. Two filling materials were applied: (1) a coarser one, with a pozzolanic effect and a maximum particle size of 400 micron as required from the 3D scans, and (2) a finer one with a filling effect, to improve the packing, the interfacial transition zone and distribution of the composed mix. The fine particles should not only improve the packing but also provide nucleation sites for increased amount of hydration products. The coarser material is supposed to act as a bridging agent between the wood wool strands. The amount of cement in this composed mix is only 30% and the latent hydraulic binder accounts for 20%.

Table 3.8: Particle size deviation compared to target line together with board density and bending strength of G (CEM I 52.5 R), a 30% GGBFS and the composed mix.

<table>
<thead>
<tr>
<th>Material</th>
<th>Deviation</th>
<th>$D_{\text{max}}$</th>
<th>$D_{\text{min}}$</th>
<th>Board density [kg/m$^3$]</th>
<th>Bending strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% G</td>
<td></td>
<td></td>
<td></td>
<td>451</td>
<td>2.40</td>
</tr>
<tr>
<td>30% GGBFS</td>
<td>543</td>
<td>60.26</td>
<td>1.1</td>
<td>414</td>
<td>2.97</td>
</tr>
<tr>
<td>Composed mix</td>
<td>115</td>
<td>150</td>
<td>0.5</td>
<td>427</td>
<td>2.60</td>
</tr>
</tbody>
</table>

From Table 3.8, it can be seen that from the three tested mixtures, the sample with 100% G has the lowest bending strength. Furthermore, when comparing the results of with 30% cement replacement by a latent hydraulic binder, a deviation of 543 µm (mainly due to coarse particles) is observed compared to the target line. It can be seen that even a latent hydraulic material has a small effect on the strength development compared to an inert filler. The “ideally” created composed mix with only 30% cement replacement resulted in a board strength of only 2.6 MPa. The results are still acceptable considering that the board only consists of 30% cement compared to the reference board.

3.5 Conclusions

In the present chapter, the upgrading and application of paper sludge fly ash (PsFA) as a cement substitute in lightweight wood wool composite board is investigated in the present study. Afterwards a second study is performed to not design a porous matrix but a matrix with lower amount of voids by optimizing the theoretical particle packing density
of the binder with the aim to increase the mechanical performance of the board and only use a small amount of cement.

PsFA is physically and chemically characterized and different treatments including a water and a combined thermal water treatment are studied. This resulted in the following samples: pre-wetted (PsFA-w); thermally at 750 °C (PSFA-h) and the thermal treated sample and then pre-wetted (PsFA h/w) to reduce its free lime content and porosity. The influence of PsFA-w on the main board properties like mechanical strength, thermal insulation, sound absorption and resistance to heat is examined. Moreover the mechanical properties of the board having an optimized particle packing are examined. Based on the obtained results, the following conclusions can be drawn:

- The high surface area (8.2 m²/g), internal pore structure (1.34 m²/g) and free lime content lead to a high water demand of PsFA. The most successful and environmentally feasible treatment route is to treat PsFA by applying a water amount of 25% of the dry mass of PsFA. This resulted in a reduction of the free lime content by an increased CaOH₂ content (8.7%), final surface area of 6.9 m²/g and internal pore structure of 0.91 m²/g.
- Replacement of the reference binder used for WWCB by 20% leads to a similar flexural strength of 3 MPa with an apparent density of 470 kg/m³. When applying 60% PsFA-w as cement replacement superior flexural strength is obtained (4.3 MPa with an apparent density of 450 kg/m³).
- Replacement of the reference binder used for WWCB by 20% reduces the board density with 50 kg/m³ and lowers the thermal conductivity up to 11.8%. When applying 60% PsFA-w as cement replacement, a low density board of 400 kg/m³ with the reduced thermal conductivity up to 17.6% is achieved.
- Replacement of the reference binder used for WWCB by 20% PsFA-w leads to an increased sound absorption by a factor of two by increasing the tortuosity and flow resistivity of the boards.
- PsFA-w provides a very good thermal profile and potential protection against the ignition of wood wool by release of chemically bound water.
- The modified Andreasen and Andersen model works also to optimize the binder layer of wood wool cement boards.
- By applying an optimized particle packing, substitution of cement by 70% mass of binder can be achieved by using a hydraulic binder (20%) and fillers (50%).
Chapter 4

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


4.1 Introduction

In the building material industry, 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 of interest as a filler, providing thermal insulation and sound absorbing properties to the host composite (Lee, 1985; Badejo, 1988; Jorge et al., 2004; Ashori et al., 2011). At the same time cement, applied as a binding agent, mineralizes the lignocellulose (Figure 4.1), adding high resistance to bio-degradation (Pereira et al., 2006b) and fire resistance (Simatupang and Geimer, 1990; Wei et al., 2000a; Doudart de la Grée et al., 2014). One example of lignocellulose inorganic mineral binder product is wood wool cement board (WWCB) with favourable mechanical, thermal and acoustical properties, applied widely in gyms, school buildings, parking garages (Glé et al., 2011; Doudart de la Grée et al., 2014; van Elten, 2015).

![Figure 4.1: Mineralised wood wool strands on different magnification levels (Caprai, 2015).](image)
The common disadvantage of the application of lignocelluloses is the inhibitory influence on the cement hydration (Wei et al., 2000a; Pereira et al., 2003; Fan et al., 2012). The leached soluble extractives from the wood withdraw water from the surrounding cement slurry and interact with Ca$^{2+}$ ions forming complexation (Doudart de la Grée et al., 2017), which consequently influence the cement hydration process. The larger the surface area of the lignocellulose particles the more the cement hardening is influenced. This is crucial for fabrication as 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 (Kochova et al., 2017). Majority of available studies deal with the cement hardening by e.g. soaking of the lignocellulose, treatment with Ca(OH)$_2$ or addition of chlorides (Pereira et al., 2006; Ashori et al., 2012; Norgren and Network, 2010). However, the influence of other parameters, e.g. volume and particle size of lignocellulose and water amount, has not been reported (Lee, 1991; Wei et al., 2000b; Ashori et al., 2011; Ashori et al., 2012).

Despite the superior performance of increased bio degradation and fire resistance of lignocellulosic composites by the cement incorporation, the increasing worldwide awareness of the substantial contribution of Portland cement (PC) to greenhouse gas emissions (Florea et al., 2014; Ramezanianpour, 2014) results in searching for alternative materials and development of new binders (Pacheco-Torgal et al., 2008; Pacheco-Torgal et al., 2012; Provis, 2014). Replacement of cement by more sustainable alternative binders will lead to a reduction of the CO$_2$ footprint. As of today, supplementary cementitious materials like coal combustion fly ash or ground granulated blast furnace slag are commonly used as cement replacement. Moreover, studies are performed on utilizing other sources of industrial by-products such as biomass fly ash, paper sludge fly ash and bottom ash. However, by increasing the substitution levels, the early strength development of the binders is drastically affected (Ramezanianpour, 2014). 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 setting and high strength development, while being more environmentally friendly (Yang et al., 2013; Ouellet-Plamondon and Habert, 2015). 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$_2$SiO$_3$, Na$_2$CO$_3$, or KOH, etc. (Yuan et al., 2015; Gao et al., 2016; Provis and Bernal, 2014; Ben Haha et al., 2011). The lignocellulose structure is prone to degrade under alkaline environment, leading to the increase of the water saturation point of the lignocellulose (Tarkow and Feist William, 1969) or changed lignocellulose microstructure (Zabel et al., 1992). Nevertheless, the degradation level depends on the alkali amount and studies on the influence of alkaline binders on the lignocellulose and application of those alternative binders in lignocellulose composites are very limited. On the other hand, pre-treating lignocelluloses with alkali like NaOH to produce ethanol and biogas has been widely studied (Budzianowski, 2016). The treatment is known to involve several physical and
ionic interaction and liquid absorption by wood in lignocellulose inorganic mineral binder composites

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 study aims to (1) understand the interactions between lignocellulose and alkaline activated binders and (2) to design a lignocellulose composite with a reduced environmental impact applying the acquired results. The study starts with the physical and chemical characterisation of the used mineral binders and lignocellulose particles in the form of wood wool strands. Then, the lignocellulose behaviour under alkaline conditions is evaluated by monitoring the pH and assessing the reactivity of the binders using an isothermal calorimeter. Next, the ionic behaviour of Ca$^{2+}$ and Na$^{+}$ in the absence and presence of lignocellulose strands is studied by ion-chromatography. In relation to the morphology of lignocellulose, the presence and position of the absorbed liquid water is studied using T$_2$ relaxometry NMR. Finally, the resulted findings are validated by designing a low CO$_2$ footprint lignocellulosic inorganic mineral-binder composite consisting of medium size wood wool particles.

4.2 Materials and Methods

4.2.1 Mineral binders

The binders used in this study are a commercial Portland cement: CEM I 52.5 R White (W) (ENCI, the Netherlands) and an one part alkali activated binder (AAB) (Van Gansewinkel Minerals, the Netherlands). In this study the one part alkali activated binder consists of industrial by products like waste and paper incineration fly ashes which are mixed with alkalis and therefore only requires water to be activated. The exact sources and mixing ratio’s of the industrial by products and alkalis cannot be provided due to confidential reasons. Finally, a ground granulated blast furnace slag (GBFS) (provided by ENCI, the Netherlands) investigated as a second AAB.

In addition to these three binders, two hybrid binders H1 and H2 are later in this study used to provide an alternative to the alkali pre-treatment. Moreover, to verify that hybrid binders are a suitable alternative to 100% W to produce lignocellulose composites. An overview of the used binders is provided in Table 4.1.

Table 4.1: Used binders in the present study.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>100% W</td>
</tr>
<tr>
<td>AAB</td>
<td>100% AAB</td>
</tr>
<tr>
<td>H1</td>
<td>70% AAB + 30% W</td>
</tr>
<tr>
<td>GGBFS</td>
<td>GGBFS</td>
</tr>
<tr>
<td>H2</td>
<td>70% GGBFS + 30% W</td>
</tr>
</tbody>
</table>
4.2.2 Lignocellulose

The used lignocellulose in this study is Norway spruce wood wool strands (Picea abies). This wood wool, produced by Knauf Insulation (the Netherlands), is commonly applied in wood wool cement boards (also known as excelsior 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 Section 4.2 and 4.4, the wood wool strands are milled to wood flour with a particle size of smaller than 400 μm to increase the inhibitory effect by generating a larger contact area.

4.2.3 Characterisation of the investigated materials

The chemical composition of the mineral binders is determined by X-ray fluorescence (XRF), together with the main cement phases calculated by using the commonly applied Bogue equations (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 N₂ adsorption, Malvern Mastersizer 2000 by means of the Fraunhofer approximation and an AccuPyc 1340 II gas Pycnometer, respectively.

The chemical composition of the wood is determined by using different techniques. The acid insoluble lignin is determined according to Tappi T222 (Tappi Method T 222 om-88, 1988) and acid soluble lignin according to Tappi UM250 (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 to obtain a 3D visualisation. Furthermore, the morphology of the binder covered wood wool is also examined by using Scanning Electron Microscopy (SEM).

4.2.4 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 on 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.

4.2.5 Isothermal calorimetry measurement

The exothermic behaviour of the binder in time is monitored in order to evaluate their 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 fixed temperature of 20 °C. The powder samples are first transferred in an ampoule and then
water or alkaline solution is added. After the addition of solution, the mixture is stirred 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.

### 4.2.6 Ionic analyses

The Ca$^{2+}$ and Na$^+$ ionic behaviour of cement, AAB and hybrid binder are evaluated in the present study. The samples are prepared by first placing 0.2 g of wood powder in a beaker and in a separate beaker a paste with a binder to water ratio by mass of 1.0. After two minutes of mixing, a homogenous paste is created. 2 g of the paste is taken 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 dissolved 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 x 250 mm) with eluent 20 mM Methasulfonic acid with an isocratic flow of 0.25 ml/min is used. The detection of ions is done by suppressed (Dionex CSRS 300 2 mm) conductivity.

### 4.2.7 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. The liquid uptake by lignocellulose has been studied (Siau, 1984) but remains complex due to the inhomogeneous microporous structure (Fourmentin et al., 2016). 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 (very) 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 (binder water mixture) by the hygroscopic cell walls and lumens of the wood.

### 4.2.8 Lignocellulose mineral binder composite design

To validate the present findings, pre-treatment of wood wool and application of an AAB or hybrid binder are evaluated by creating a lignocellulose mineral binder composites with dimensions of 20 x 15 x 1.5 cm$^3$ (Figure 4.2). The preparation procedure can be found elsewhere (Doudart de la Grée, 2014).
Boards are produced using AAB and GGBFS to evaluate the alkali treatment of the wood wool and a board made of W is used as a reference (Table 4.2). Next H1 and H2 are evaluated (B4 and B5 in Table 4.2). Further, tests are performed to H1 to study the effect of wood to liquid amount, with a range between 3.45-1.97 (B6 - B8 in Table 4.2) which are examined using SEM. A complete overview of the boards is provided in Table 4.2. Boards are considered to be satisfactory when a minimum flexural strength of 1.7 MPa is achieved after 10 days of curing with a target density of 400 kg/m$^3$ (Mencnarowski, 2014).

**Table 4.2**: Tested board recipes and evaluated wood to water ratios.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binder</th>
<th>Water-to-binder ratio</th>
<th>Wood-to-binder ratio</th>
<th>NaOH/binder ratio</th>
<th>Na$_2$SiO$_3$/binder ratio</th>
<th>Wood-to-pretreatment liquid-ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>W</td>
<td>0.50</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>2.30</td>
</tr>
<tr>
<td>B2</td>
<td>AAB</td>
<td>0.50</td>
<td>0.75</td>
<td>0.1</td>
<td>-</td>
<td>2.30</td>
</tr>
<tr>
<td>B3</td>
<td>H1</td>
<td>0.50</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>2.30</td>
</tr>
<tr>
<td>B4</td>
<td>GGBFS</td>
<td>0.50</td>
<td>0.75</td>
<td>0.26</td>
<td>0.2</td>
<td>2.30</td>
</tr>
<tr>
<td>B5</td>
<td>H2</td>
<td>0.50</td>
<td>0.75</td>
<td>0.035</td>
<td>0.14</td>
<td>2.30</td>
</tr>
<tr>
<td>B6</td>
<td>H1</td>
<td>0.50</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>3.45</td>
</tr>
<tr>
<td>B7</td>
<td>H1</td>
<td>0.50</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>2.30</td>
</tr>
<tr>
<td>B8</td>
<td>H1</td>
<td>0.50</td>
<td>0.75</td>
<td>-</td>
<td>-</td>
<td>1.97</td>
</tr>
</tbody>
</table>

**Figure 4.2**: Flexural test on lignocellulose composite boards with the evaluated board dimensions and a cross section of a covered wood wool strand with a layer of cement in 3D CT scan (Doudart de la Grée, et al. 2014).

### 4.2.9 Environmental impact

To evaluate the sustainability of the created lignocellulose mineral binder composites, the CO$_2$ footprints of the binder mixtures are evaluated. The CO$_2$ footprint of the wood wool is not taken into account since the type and amount of wood wool is not changed. For the CO$_2$ footprints of the binder mixtures, values of CO$_2$ footprints per component of the
binder and the activator are taken into account. These values have been retrieved from available literature (Collins, 2010; Turner and Collins, 2013) and data provided by van Gansewinkel (Keulen, 2015), as presented in Table 4.3. Although the CO₂ footprint value could only be obtained for G (CEM I 52.5 R) the used cement type is W (CEM I 52.5 R White). In case of W, the lower amount of C₄AF in the clinker requires a higher temperature in the kiln, hence, the CO₂ footprint will be even higher than the one reported for G and is in this study only used as an indication of an improvement since a complete white appearance is with the used AAB not possible.

Table 4.3: CO₂ footprint of the used binder ingredients (Collins, 2010; Turner and Collins, 2013; Keulen 2015).

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>kg CO₂eq per kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binder</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>0.82</td>
</tr>
<tr>
<td>AAB</td>
<td>0.10</td>
</tr>
<tr>
<td>GGBFS</td>
<td>0.143</td>
</tr>
<tr>
<td>Activators</td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>1.915</td>
</tr>
<tr>
<td>Na₂SiO₃</td>
<td>1.514</td>
</tr>
</tbody>
</table>

4.3 Results and discussion

Minerals

The chemical composition of the binders is determined by X-ray fluorescence (XRF) and the results are shown in Table 4.4. By using the Bogue equations, the main cement phases of CEM I 52.5 R white (W) are computed. It is shown that the W contains a high C₃A content of 10% and C₅S content of 80% compared to a CEM I 52.5 R of ~7% and ~56% (Doudart De la Grée et al., 2015), respectively as well as a similar gypsum content of approximately 3%. Moreover, W contains almost no C₄AF (negligible amount of 1%), in order to ensure the white appearance. The one part alkali activated binder (AAB) 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% SO₃, which ensures that it can be activated with the addition of only water. Its SiO₂/Na₂O 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 (Bai et al., 2003; Mozaffari et al., 2009). The GGBFS (Solid precursor) has a moderate content of CaO which is derived from CaCO₃ 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 Na₂SiO₃ activator, C-A-S-H gels are generated. The Na₂SiO₃ solution is composed of 27.69% SiO₂, 8.39% Na₂O and 63.9% H₂O by mass and together with NaOH leads to a high initial pH of ~13.2 and adjusted SiO₂/Na₂O ratio (Skorina and Tikhomirova, 2012). The physical properties of the used binders are listed in Table 4.5.
Table 4.4: Chemical composition of the applied binder compounds in [%].

<table>
<thead>
<tr>
<th>Materials [%]</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>SO$_3$</th>
<th>MgO</th>
<th>TiO$_2$</th>
<th>Mn$_3$O$_4$</th>
<th>P$_2$O$_5$</th>
<th>Other oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>67.19</td>
<td>20.86</td>
<td>3.91</td>
<td>0.45</td>
<td>0.12</td>
<td>0.11</td>
<td>2.92</td>
<td>0.40</td>
<td>0.33</td>
<td>0.02</td>
<td>0.51</td>
<td>3.18</td>
</tr>
<tr>
<td>AAB</td>
<td>42.24</td>
<td>23.45</td>
<td>9.68</td>
<td>6.73</td>
<td>0.73</td>
<td>1.92</td>
<td>6.95</td>
<td>6.41</td>
<td>0.69</td>
<td>0.20</td>
<td>0.34</td>
<td>0.66</td>
</tr>
<tr>
<td>GGBS</td>
<td>38.89</td>
<td>34.18</td>
<td>13.63</td>
<td>0.51</td>
<td>0.43</td>
<td>0.33</td>
<td>1.41</td>
<td>10.62</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.5: BET specific surface areas, specific density ($\rho_s$) and the mean particle size of the used binders.

<table>
<thead>
<tr>
<th>Binder</th>
<th>BET surface area [m$^2$/g]</th>
<th>$\rho_s$ [g/cm$^3$]</th>
<th>$D_{50}$ [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>1.21</td>
<td>3.11</td>
<td>16.90</td>
</tr>
<tr>
<td>AAB</td>
<td>3.67</td>
<td>2.92</td>
<td>25.00</td>
</tr>
<tr>
<td>GGBS</td>
<td>1.70</td>
<td>2.89</td>
<td>30.00</td>
</tr>
</tbody>
</table>

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 4.6, indicating proper reactions and mechanical strength properties in the absence of wood.

Table 4.6: Mortar recipes with compressive strength results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binder</th>
<th>Binder [g]</th>
<th>Water [g]</th>
<th>Sand [g]</th>
<th>NaOH [g]</th>
<th>Na$_2$SiO$_3$ [g]</th>
<th>1 day Compressive strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W</td>
<td>450</td>
<td>225</td>
<td>1350</td>
<td>-</td>
<td>-</td>
<td>22</td>
</tr>
<tr>
<td>2</td>
<td>AAB</td>
<td>450</td>
<td>225</td>
<td>1350</td>
<td>-</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>H1</td>
<td>450</td>
<td>225</td>
<td>1350</td>
<td>-</td>
<td>-</td>
<td>17</td>
</tr>
<tr>
<td>4</td>
<td>GGBFS</td>
<td>450</td>
<td>168.3</td>
<td>1350</td>
<td>22.5</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>H2</td>
<td>450</td>
<td>168.3</td>
<td>1350</td>
<td>15.75</td>
<td>63</td>
<td>27</td>
</tr>
</tbody>
</table>

W is commonly applied in wood wool cement composites production due to its white appearance. Furthermore, high contents of C$_3$A and C$_3$S promote the early strength development of the binder (1 day compressive strength of 22 MPa, see Table 4.6), therefore suppressing the inhibitory effects when mixing with lignocellulose. AAB is a one part alkali-activated binder consisting of industrial by-products. The binder has a slower reaction compared to W, leading to a 1 day compressive strength of 14 MPa. Nevertheless, AAB is of interest since: (1) the reaction process is occurring at a pH ~12.5 which is lower compared to other AAB systems (pH 13+) and therefore increases the compatibility with wood (cement, pH 12 is already successfully applied for years); (2) it consists of minerals as a residue from the recycling industry. H1 is evaluated to enhance the activation of AAB 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. GGBFS is an alkali activated slag, achieving a high compressive strength of 30 MPa after 1 day (Pacheco-Torgal et al., 2008; Gao et al., 2016). H2 is evaluated to stabilize the pH as is the case for H1 having a 1 day compressive strength of 27 MPa.
Wood wool strands

The chemical composition of the wood wool strands is presented in Table 4.7. Monosaccharides usually have a pKa of 12 (Rovio et al., 2007) while the galacturonic and glucuronic acids have a pKa around 3.4 (Kohn and Kováč, 1978), leading to neutralization reactions in an alkaline environment. 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, glucomannan) that 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.

Table 4.7: Chemical composition of the used spruce wood wool strands in [%] (Merta, 2014).

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

The porous microstructure of the wood wool is presented together with a strand covered with and without a binder (Figure 4.2 and Figure 4.3) (Doudart de la Grée, et al., 2014). Hexagonal shaped pores with a length of 120 μm and width of 40 μm are identified (Figure 4.3a) and the porosity of the wood wool is about 63%. The picture shown in Figure 4.3a illustrates the high porosity of the wood wool. The thickness of this binder layer ranges between 40-140 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 are found to be very hygroscopic and are 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). The used wood flour in this study is visualised in Figure 2b for clarification.

![Spruce wood wool strands](image)

![Cross section of wood wool strands](image)

![Flour wood wool (PSD < 400 um)](image)

![Longitudinal section of wood wool strands](image)

**Figure 4.3**: (a) Spruce wood wool strand with a cross section of the wood wool strands and a longitudinal section of wood wool (Caprai, 2015); (b) Used wood wool flour created by milling the spruce wood wool.

### 4.3.1 Behaviour of wood wool under alkaline conditions

Figure 4.4 shows the evolution of the pH of an alkaline medium (water + NaOH) containing wood wool strands over time. It is evident that wood wool leads to the reduction of the initial alkalinity of the system (pH 13.5-12) by different mechanisms. In an alkaline environment the main wood components, presented in Table 4.8, can be degraded (ester bond cleavage and peeling reactions) (Sjöström, 1993, 1977), leading to smaller fragments of organic acids (e.g. formic, acetic and hydroxyacids) as presented in Table 4.8. The degradation of the reducing end-groups (peeling reaction) consumes OH⁻ (Pavasars et al., 2003; Loon and Glaus, 1997). 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).
Figure 4.4: pH behaviour of spruce wood wool strands under various starting pH conditions.

Table 4.8: Alkaline degradation of lignocellulosic components with an example of formed products.

<table>
<thead>
<tr>
<th>Components</th>
<th>Reactions under alkaline conditions</th>
<th>End products</th>
<th>Interaction of end products with system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>Peeling reaction (Loon and Glaus, 1997; Pavasars et al., 2003) Chemical termination (Loon and Glaus, 1997; Pavasars et al., 2003)</td>
<td>Metasaccharinic acid (Loon and Glaus, 1997; Pavasars et al., 2003) Isoaccharinic acid (Loon and Glaus, 1997; Pavasars et al., 2003)</td>
<td>Neutralisation reaction</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>Breaking down of Ester bonds (Sjöström, 1993)</td>
<td>Carboxylic acids and Alcohols Phenolics</td>
<td>Neutralisation reaction</td>
</tr>
<tr>
<td>Lignin</td>
<td>Alkaline hydrolysis (of acetyl groups and esters) (Sjöström, 1977) Removal of soluble lipids &amp; carbohydrates (sugars)</td>
<td>Phenolics</td>
<td>Interaction with reaction products</td>
</tr>
<tr>
<td>Acids</td>
<td>Neutralisation reaction</td>
<td>Fatty acids and Complexation with cations glycerol (saponification)</td>
<td></td>
</tr>
</tbody>
</table>

In the period of 4 h, 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⁻ 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 drop of pH, needed for the binder to react, an equivalent amount of OH⁻ ions is added to the system as will be discussed in Section 4.3.5 to achieve the optimum pH conditions.
4.3.2 Reaction kinetics of the binders

In Figure 4.5, 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 W, AAB and H1 differ. W maintains a stable pH of 12 in time, having a lower dissolution peak in the first 1 h compared to the other binders (Figure 4.5b). The high pH of W is attributed to the fast dissolution of the cement phases C₃A, C₄AF and C₃S releasing Ca²⁺, Al³⁺, Fe³⁺ and OH⁻ ions. Afterwards a low reaction of the cement occurs up to 4 h (Figure 4.5b and 4.5c), and the pH stays stabilized. After the induction period, the ions in the liquid start to form the hydration products in the form of C-S-H and Ca(OH)₂ and the remaining phases continue to react, as observed by the continued liberation of heat.

Both AAB and H1 have initially a high pH because of the dissolution of alkalis releasing OH⁻ ions, as confirmed by Figure 4.5b and 4.5c. 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). Note 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 H1 remains constant (around 12) due to the implementation of 30% cement acting as a buffer. The heat release of H1 compared to AAB in the first 24 h is lower due to the presence of cement (liberates less heat in the first 15 h) but gradually in time liberates heat by formation of reaction products as seen for W (Figure 4.5c).

![Figure 4.5](image)

Figure 4.5: (a) pH behaviour in time of W, AAB and H1; (b) Normalized heat flow of binders; (c) Normalized heat of the binders.

4.3.3 Ionic uptake of wood and alteration of binder reaction mechanism

As described in Sections 4.1 and 4.2, wood has the tendency to absorb ions from the cement paste, neutralizing the pH. This is investigated for W, AAB and H1 on two cations Ca²⁺ and Na⁺ using ion chromatography. The ion concentration in time (ionic behaviour) of Mix 1 (containing W) and Mix 2 (containing AAB) is shown in Figure 4.6.
Figure 4.6: Ionic behaviour of (a) Mix 1 (without wood) and Mix 1 W (containing wood); (b) Mix 2 (without wood) and Mix 2 W (containing wood).

Figure 4.6 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$_3$S amount present. However, other researchers who measured the Ca$^{2+}$ in the first 1-4 h described a slow decrease in concentration (Singh et al., 1995; Rai et al., 2004). 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; Hon and Shiraishi, 2000; 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 two hours 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 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\textsuperscript{+} concentrations are significantly lower after 4 h. On the other hand, the Ca\textsuperscript{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.

Based on the results of Mix 1 and Mix 2, a hybrid binder consisting of AAB and cement (H1) is studied to investigate the effect of cement on providing additional Ca\textsuperscript{2+} and OH\textsuperscript{-} ions, which leads to a more stable and prolonged reaction. The ionic behaviour of Ca\textsuperscript{2+} and Na\textsuperscript{+} in Mix 3 (containing H1) is presented in Figure 4.7. When wood is present, the Ca\textsuperscript{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\textsuperscript{2+} concentration starts to fluctuate by the dissolution of cement, which provides Ca\textsuperscript{2+} that favours the formation of a C-A-S-H gel compared to N-A-S-H.

![Figure 4.7: Ionic behaviour of the Mix 3 and Mix 3 containing wood (Mix 3 W).](image)

To summarize, it is clear that the ionic behaviour in the presence of wood strongly depends on the reaction mechanism of the used binders (Figure 4.8) as mentioned in (Provis, 2014; Gao et al., 2015). W is able to react and stabilize the pH by providing OH\textsuperscript{-} and Ca\textsuperscript{2+} ions, leading to a continuous reaction, whereas the alkaline binder (AAB) rapidly loses OH\textsuperscript{-} ions, due to the interaction with wood. In order to reduce this influence, a replacement of the alkaline binder by 30% cement (H1), acting as a buffer to provide OH\textsuperscript{-} and Ca\textsuperscript{2+} ions, enables the further reaction.
4.3.4 Position of the absorbed water in wood wool strands

Figure 4.9a presents the proton NMR spin-spin relaxation time ($T_2$) spectra of the investigated wood wool strands with different moisture contents to identify the bonding trends and location of liquid water when pre-treating the wood as visualised in Figure 4.9b. These results are also published elsewhere (Caprai et al., 2018). Wood strands with a moisture content ($M_c$) of 11% (by dry mass of wood) shows only one peak at a relaxation time $T_2$ less than 1 ms, attributed by hydrogen bonded water in the cell walls. When increasing the moisture content to 50 and then to 70%, a second and third peak is visible. The first peak related to the water in the cell walls shifts to the right, leading to a higher relaxation time of >1 ms (Felby et al., 2008). The second peak is related to the water in the lumen by capillary forces and 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 indicates the position of surface water, with a relaxation time of 50 ms. The total peak height and the area beneath the curve are increased for $M_c$ 70% compared to $M_c$ 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 150%. While removing the surface water, e.g. with an absorbing paper, results in the disappearance of the third peak (see sample 150 $M_c$ sd in Figure 4.9a), which confirms that the third peak positioned at 50 ms is attributed to the surface water.
Figure 4.9: (a) T2 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 (Caprai, 2015)

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, 2011a). 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.

4.3.5 Evaluation of pre-treatment

Based on the obtained results in the present research, a design of a sustainable lignocellulosic mineral-binder composite is performed to evaluate the pre-treatment effect. Two treatment routes are investigated to compensate the alkali consumption by: (1) Pre-treating the wood wool with an alkaline solution and applying the AABs (AAB and GGBFS); (2) Pre-treating the wood wool with water, but applying a hybrid binder (H1 and H2). The alkali pre-treatment is designed based on the pH reduction presented in Figure 4.4 of Section 4.3.1. For the AAB a NaOH concentration of 8.5% based on dry wood is added to the system (starting pH 13) and for alkali activated slag (GGBFS) 28.5% (starting pH 13.5), both with an Mc of 60%.

Table 4.9: Overview of Mc, apparent density (ρb) and flexural strength of the evaluated boards.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Binder</th>
<th>Mc wood*</th>
<th>ρb [kg/m³]</th>
<th>Flexural strength [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>B1</td>
<td>W</td>
<td>60</td>
<td>399</td>
<td>1.9</td>
</tr>
<tr>
<td>B2</td>
<td>AAB</td>
<td>60</td>
<td>388</td>
<td>1.8</td>
</tr>
<tr>
<td>B3</td>
<td>H1</td>
<td>60</td>
<td>357</td>
<td>1.6</td>
</tr>
<tr>
<td>B4</td>
<td>GGBFS</td>
<td>60</td>
<td>420</td>
<td>2.3</td>
</tr>
<tr>
<td>B5</td>
<td>H2</td>
<td>60</td>
<td>430</td>
<td>2.0</td>
</tr>
<tr>
<td>B6</td>
<td>H1</td>
<td>50</td>
<td>404</td>
<td>1.0</td>
</tr>
<tr>
<td>B7</td>
<td>H1</td>
<td>60</td>
<td>428</td>
<td><strong>3.1</strong></td>
</tr>
<tr>
<td>B8</td>
<td>H1</td>
<td>70</td>
<td>413</td>
<td>1.8</td>
</tr>
</tbody>
</table>

*Pre-treatment moisture content based on oven dry mass of the wood
The flexural strength results of all samples are listed in Table 4.9. The samples using W (B1), AAB (B2) and GGBFS (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 H1 (B3) and H2 (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 4.9 illustrates the flexural strength of composites using H1 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% (Figure 4.10b). It is revealed by SEM that a proper reaction did not occur when applying a $Mc$ of 50% (Figure 4.10a), while a high $Mc$ value of 70% indeed results in an increase of the porosity by the diluting effect (Figure 4.10c), 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.
Figure 4.10: SEM pictures of boards made with H1 using 2.0 mm width strands (a) 50%; (b) 60%; (c) 70% pre-treatment moisture content (Caprai, 2015).

4.3.6 Environmental impact
For AAB, the low CO₂ footprint of the binder positively reduces the CO₂ footprint by 72.9% (Table 4.10) despite the NaOH pre-treatment. For H1, no alkali pre-treatment is required but the use of 30% cement leads to a slight increment of the CO₂ footprint
compared to AAB, but is still 61.5% lower compared to W. Application of GGBFS with an NaOH and Na₂SiO₃ and an alkali pre-treatment leads currently to an increase of the CO₂ footprint compared to W by 16.0%, which is attributed to the significant amount of NaOH used to pre-treat the wood wool (Table 4.2). 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 H2, the hybrid binder containing alkali activated slag and cement requires no pre-treatment, achieving a 23.8% reduction of the CO₂ footprint hence, a proper pre-treatment is essential in successfully applying the alkali activated binder in such lignocellulose based environment.

Table 4.10: Environmental consideration.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Pre-treatment</th>
<th>total CO₂ eq. per kg of mixture</th>
<th>total CO₂ eq. per kg of treatment</th>
<th>CO₂ footprint composite %</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>water</td>
<td>0.150*</td>
<td>-</td>
<td>Ref</td>
</tr>
<tr>
<td>AAB</td>
<td>NaOH</td>
<td>0.018</td>
<td>0.022</td>
<td>-72.9</td>
</tr>
<tr>
<td>H1</td>
<td>water</td>
<td>0.058</td>
<td>-</td>
<td>-61.5</td>
</tr>
<tr>
<td>GGBFS</td>
<td>NaOH</td>
<td>0.099</td>
<td>0.075</td>
<td>+16.0</td>
</tr>
<tr>
<td>H2</td>
<td>water</td>
<td>0.115</td>
<td>-</td>
<td>-23.8</td>
</tr>
</tbody>
</table>

* The calculated CO₂ eq per kg for binder W was not available. Therefore, the CO₂ eq per kg for binder G is used in this study as an indication as explained in Section 4.2.9. The CO₂ footprint of W is due to its burning process higher, meaning that the obtained CO₂ reductions are also higher.

4.4 Conclusions

This study addresses the interaction between alkali activated binders and lignocellulose wood wool strands. The behaviour of lignocellulose under different alkaline environment and the effect of lignocellulose on the ionic behaviour of Ca²⁺ and Na⁺ in different binders are studied. The microstructure, treatment of wood wool and position of absorbed liquid in wood wool are studied. The present findings lead to the design of a sustainable wood composite with excellent properties. Furthermore, the environmental impact of the investigated binders are analysed. 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, hence, reactivity of alkali activated binder is negatively affected.
- The ionic uptake of wood results in insufficient reaction of the alkali-activated binder that can be compensated by additional OH⁻ and Ca²⁺ ions from an alkali pre-treatment or substitution of the alkali activated binder by cement.
- The NMR results indicate that an addition of 60% water on dry mass of wood is sufficient to pre-treat the wood wool, resulting in the highest mechanical properties.
- Application of 100% alkali-activated binder with proper initial pH or a hybrid binder demonstrate very promising results, especially indicated by a remarkable CO₂ footprint reduction by 72.9% and 61.5% compared to a pure cement system.
Advanced functionalities

5.1 Introduction

In recent years, there is an increased awareness of the risk of health problems when exposed to improper indoor and outdoor air quality. To establish a healthy indoor and outdoor air quality, measures to reduce the level of pollutants are required. The type of measures required depends on the type of pollutants since they can be present in different forms like airborne particulate matter (PM) or gaseous air pollutants e.g. volatile organic compounds and inorganic compounds. PM concentrations in indoor buildings can already be reduced when filtration of the air is applied which is incorporated into combustion and ventilation systems. The removal of air pollutants by using photocatalytic oxidation systems (PCO) is by its novelty less extensively in practice applied and is still a studied matter.

At the same moment, the acceptance of a material is increased when it has the ability to satisfy multiple requirements. A material including different attributes results more suitable for various conditions and special applications. Because WWCB has a high surface area, low flow resistivity and can be applied both indoor and outdoor, it is a potential carrier for PCO. The present chapter addresses the potential of WWCB as an air purifying material by applying photocatalytic oxidation using NO as the target pollutant. Different WWCB with various surface structures and binders under various airflows are studied and exposed to a water treatment to determine the suitability and adhesion of the PCO to the substrate. A schematic representation of the chapter is provided in Figure 5.1.

![Schematic representation of this study](image)

**Figure 5.1**: Schematic representation of this study in which (a) represents the working mechanism of a photocatalyst; (b) The surface characteristics of WWCB; (c) Influencing parameters for NO$_x$ degradation like surface roughness, airflow and adhesion properties of the substrate on the support.
5.2 Air quality

5.2.1 Introduction
The risk of affecting the human health by air pollution is known since centuries. Natural air pollution by forest fires, eruption of volcanoes (Figure 5.2a) and biological decay are three examples occurring all over the world involving gasses of sulphur dioxide (SO$_2$), nitrogen oxides (NO) and the production of volatile organic compounds (VOCs) from plants and trees. Besides these gasses, also particulate matter transported in air over large distances from volcanoes or dust storms count for air pollution with particle sizes varying between 2.5 to 25 µm (Navrátil et al., 2013). In high quantities, under long exposure and depending on the health status of susceptible individuals, these gases can lead to serious health issues (McLaren and Williams, 2015). Although the natural air pollution occurs continuously by natural events during the dawn of time, man-made air pollution caused by human activities started to evolve during the industrial revolution (Simkhovich, et al., 2008) observed by major increasing records of deaths, hospitalized people and fog which paralyzes entire cities. Nowadays, the vast majority of pollution affecting human society originates from human activities and therefore is susceptible to the human control and legislative activities. The population growth is increased by a factor two since 1950 (Fenger, 1999) and the industrial development led to area’s with a denser concentration of people (urbanization). These two aspects are accounted for the two main factors of the increased modern concerns about air pollution known as urban air pollution. On the other hand, the industrial revolution and pollution was in that period of time perceived as a symbol of wealth and growth advertised on pictures with chimney stacks and cars with visible exhaust (Fenger, 1999). Since the year 2000, 3000 different anthropogenic air pollutions have been identified. The sources of air pollution are mainly related to the combustion of fossil fuels for industrial processes (Figure 5.2b), generation of electricity and mobile sources for transportation like cars, trucks, railroad trains, airplanes etc. Smaller amounts of pollutants are released from wide scalar of activities in the daily life like cooking and smoking. The health risk related to air pollution is estimated to 7 million premature deaths (according to the World Health Organization), caused by a variety of effects like infections, heart diseases, stroke and lung cancer recognized by difficulty in breathing, wheezing, coughing and asthma. Therefore, it is of vital importance to reduce the air pollution to improve both indoor and outdoor air quality.

![Figure 5.2: (a) Natural air pollution by the eruption of Mount Pinatubo in 1991 (Bourseiller, 1991); (b) Industrial pollution by factories in Wuhai city Mongolia in 2005 (Guang, 2015).]
The reduction of air pollution can be achieved by minimizing the use of fossil fuels and making the transition to renewable energy sources like wind, solar and hydro power to produce electricity allowing for instance the utilization of electric vehicles. Another solution which is still under investigation and less known is the utilization of titanium dioxides (TiO\textsubscript{2}) to reduce air pollution by creating free radicals which decompose VOCs and NOx gases.

5.2.2 Indoor and outdoor air pollutants

Various international and/or national standards and recommendations are set to guide the air quality and one of them is the world health organization (WHO). Considering gas pollutants there is a distinction between organic and inorganic gas pollutants.

**Organic air pollutants**

Typical organic air pollutants like benzene, formaldehyde, toluene etc. are emitted from different combustion processes such as tobacco smoke, and benzene-containing petrol. Among the organic air pollutants, volatile organic compounds (VOCs) especially cause health problems for human being. VOCs can originate from many sources such as paints, paint strippers and other solvents, wood preservatives, aerosol sprays, moth repellents and air fresheners, building materials and furnishings, printers and permanent markers etc. VOCs include a variety of chemicals which have short or long term adverse health effects and are in a higher concentration present indoor compared to outdoor air. For instance, the United States Environmental Protection Agency reported 2 to 5 times greater indoor air concentration compared to outdoor air. Immediately after certain activities such as paint stripping, levels may be 1000 times higher compared to outdoor levels (EPA, 2016). The risk of indoor air pollution can only be reduced when having source control of pollutants e.g. limiting the chemical emissions in the indoor environment, proper ventilation and effective cleaning and maintenance preventing mold growth.

**Inorganic air pollutants**

Classical inorganic gas pollutants include nitrogen oxides, carbon monoxide, sulfur dioxide, etc. Nitrogen oxides (NOx) are formed by oxidation of atmospheric nitrogen coming from fuel combustion of cars and industrial power plants and are emitted in the form of nitric oxide (NO), which is subsequently oxidized in the atmosphere to the secondary pollutant NO\textsubscript{2}. On ground level NO react with oxygen to form ozone but NO\textsubscript{2} can also decompose when is in contact with water to form nitrous acids (HNO\textsubscript{2}) and nitric acid (HNO\textsubscript{3}). This acid (known as acid rain) is destructive to anything it is in contact with. The emissions of NOx can be reduced by optimization of the combustion process (low NO\textsubscript{x} burners in power plants and lean burn motors in motor vehicles) of by means of catalytic converters in the exhaust (Fenger, 1999). Carbon monoxide (CO) is formed when carbon in fuel is not completely burned causing serious health effects on humans since CO reacts with the hemoglobin in our blood streams and therefore prevents oxygen from entering the body (hemoglobin is an oxygen binding protein). CO can be lethal when the concentration is higher than 750 ppm (Sivashanmugam, 2007). Sulfur dioxide is mainly associated with sulphur in fossil fuels and the burning of coal and can
be reduced by using fuels with low sulphur content or using a desulphurization techniques.

5.2.3 Additional functionalities

The value of a material increases when it has the ability to satisfy multiple requirements. A multifunctional material is a material which possess attributes beyond the basic properties that typically drives the engineering of the material. Designing of a material by incorporating more functionalities can occur through the modification of their chemical composition or by implementing additional compounds. This can bring numerous benefits, e.g. reduction of costs, size and weight, utilization options as well as ecological impact. Simultaneously also safety, adaptability, efficient use of raw materials and durability can be raised (Nemat-nasser et al., 2005).

Analyzing a wood wool cement composite, the material possesses already a number of functionalities because of the collaboration between wood wool strands covered by hardened cement. An additional functionality can be air purification to reduce the air pollutants, by introducing a photo-catalyst. A photo-catalyst could be applied both as additive in cement matrixes and as coatings, since the photo-catalytic process may occur at air-solid interface as well as at liquid-solid interface (Carp, 2004). The technique of using photocatalytic materials for air purification is promising because it is more cost efficient compared to current purification methods (Hendrix et al., 2015). However, the design of a multifunctional material is not straightforward and requires understanding of physical and chemical mechanisms to require specific properties. Fortunately WWCB is a material that offers great flexibility in tailoring specific properties by controlling its composition e.g. wood volume, cement volume and by that its microstructural properties.

5.3 Photocatalytic oxidation

5.3.1 Introduction

Among the widespread photo-catalyst, titanium dioxide (TiO$_2$) and zink oxide ZnO are the most commonly applied for photo-catalytic oxidation systems (PCO). It is able to decompose a wide range of pollutants and it does not need the addition of any other compound (Hager et al., 2000). PCO is not only able to reduce the amount of air pollutants in the outdoor environment but can also be applied indoors, enable lower ventilation rates in buildings, hence, a lower energy use, due to a less polluted indoor air (Hashimoto et al., 2005). The covering, characterized by nano-semiconductor catalysts, is activated by UV and visible light. The working mechanism, and known applications will be further introduced in this paragraph.

Hager et al. (2000) states that TiO$_2$ is the most advantageous photo-catalyst, because of its superior characteristic:

1) It does not need the addition of any other compound;
2) It is stable, despite of its high photo-catalytic efficiency;
3) It is able to provide an oxidation at ambient temperature, for most of the indoor air pollutants;
4) A wide range of pollutants could be oxidized.

Furthermore, the crystalline structure and the possible application on heterogeneous support materials enhance the TiO$_2$ efficiency (Zhao and Yang, 2003). In this the band gap of the material plays an important role, since it determines the minimum energy of light required to make the material electrically conductive.

The main crystal phases of this oxide are anatase and rutile. Both belonging to the tetragonal crystal system, anatase phase has higher photo-catalytic efficiency than rutile. The higher performance depends on the number of electrons around the Fermi energy, at the anatase phase. The photo-catalytic activity of TiO$_2$, is proportional to the number of electrons delivered by the UV ray. The probability of this emission depends on the electrons density near Fermi energy. Hence, a phase, as anatase, with higher density of particles will have a higher photo-catalytic activity (Park et al., 2009). In contrary to the rutile phase, the anatase provides stable surface peroxide group, during the photo-oxidation.

During the photo-oxidation, the activity of the photo-catalytic compound is strongly affected by the type and amount of hydroxyl groups. Therefore, the decrease of the amount of hydroxyl groups, during the photoreaction, reduces the efficiency of the catalyst.

Light is one of the main components in the photo-catalytic reaction. The absorption of the light with specific threshold wavelength could supply the energy necessary to overcome the band gap between valence bands and conduction bands. Reaching the right activation energy, the electrons are able to move between valence bands and conduction bands, creating hole-electron pairs on the TiO$_2$ surface.

5.3.2 PCO working principle

The air purification techniques of PCO combine the nano-semiconductor catalysts and the UV light to transform VOC and inorganic compounds like NOx, in indoor air into innocuous and odourless constituents, such as CO$_2$ and H$_2$O (Mo et al., 2009). In the PCO reaction, pure or doped semi-conductors, such as TiO$_2$, ZnO, CdS, Fe(III)-doped TiO$_2$ are usually used as photo-catalysts. Commonly used light sources are Ultra-violet (UV) lights, such as fluorescent black-light (300-370 nm). However, there are also visible responsive photo-catalysts (Mo et al., 2009). The chemical reaction takes place, due to the exposition of the photo-catalyst to UV-ray/visual light (hv), generating oxidizing and reducing agents. During the process, the light on the valence band causes electrons to excite from the valance band into the conduction band causing the creation of positive holes inside it. Their presence, together with the electrons, drives oxidation and reduction process of external agents, located on the surface of the photo-catalyst. Figure 5.3 displays graphically this process.
Yu (2011) expressed the activation mechanism as:

\[ TiO_2 + h\nu \rightarrow e^- + h^+ \]  \hspace{1cm} (5.1)

Where \( h^+ \) is the oxidation agent and \( e^- \) is the reducing agent. The primary oxidant and reduction reaction are described as

Oxidation reaction:

\[ h^+ + H_2O \rightarrow OH^* + H^+ \]  \hspace{1cm} (5.2)

Reduction reaction:

\[ e^- + O_2 \rightarrow O_2^- \]  \hspace{1cm} (5.3)

Where \( OH^* \) is the hydroxyl radical and the primary oxidant.

From the equations it is evident that the absorbed oxygen and water play a vital role in the photocatalytic reaction where the oxygen is used to trap the generated electrons on the \( TiO_2 \). With NOx as pollutant, the following mechanisms of absorption and oxidation of NOx are occurring:

\[ NO + OH^* \rightarrow HNO_2 \]  \hspace{1cm} (5.4)
\[ HNO_2 + OH^* \rightarrow NO_2 + H_2O \]  \hspace{1cm} (5.5)
\[ NO_2 + OH^* \rightarrow NO_3^- + H^+ \]  \hspace{1cm} (5.6)

### 5.3.3 Application of PCO

Air purification by successful incorporation of a photocatalytic material in building materials like concrete, wallpaper, gypsum and paint are summarized in Hendrix et al. (2015). Besides the positive influence of air purification, application of \( TiO_2 \) for wood related products reduces the risk of algae, fungus, mildew and mold growth which can occur on WWCB products (see Figure 5.4).
5.4 Air purifying WWCB

5.4.1 Introduction
The possible success of applying a photo catalyst on WWCB is related to its high surface area (SA) that enables the coating to be widely distributed (high active surface) and high surface roughness (SR) with an interconnected pore structure that enables a high mass transfer. The open structure of the board is created by the overlapping of disorganized wood wool strands, which allows the air passing through the material. Furthermore, the support mainly consist of wood and enables moisture uptake and release by its hygroscopic property which can be beneficial for the degradation of pollutants. In this paragraph the influential parameters, the used support and test set-up are introduced.

5.4.2 Influential parameters

Light
Light is one of the main components in the photo-catalytic reaction. The absorption of the light with specific threshold wavelength could supply the energy necessary to overcome the band gap between valence bands and conduction bands. Reaching the right activation energy, the electrons are able to move between valence bands and conduction bands, creating hole-electron pairs on the TiO₂ surface. Although the UV wavelength seems to be the most suitable range to start the photo-catalytic reaction (between 300-370 nm) also visible light can be used in the range of (400-700 nm). For this, a pre-treatment is required that is enhancing the photo-catalyst performances. The main process are:

1) Doping the TiO₂ with transition metal ions;
2) Doping nitrogen into TiO₂ and using sensing dyes.

The former treatment extends the light absorption into the visible region. The metal ions, behave as recombination sites for the photo-generated charges carriers. Beneficial effects are brought by metals ions, such as Li⁺, Zn₂⁺, Cd₂⁺, Ce³⁺, Co³⁺, Cr³⁺, Fe³⁺, Al³⁺, Mn²⁺.
Furthermore, metal ions increase the elimination of electron-hole recombination, in the photo-catalytic reaction, as they can couple with other semiconductors, into the catalyst. The height of the performance also depends on the catalyst structure. The addition of ZrO$_2$ into TiO$_2$-xN$_x$ generates a higher porosity and high specific surface area, improving the thermal stability of the material. Furthermore, the use of dye in case of semiconductors with high band-gap, loads the electron-transfer process, in the photo-reaction (Mo et al., 2009).

Hunger and Brouwers, (2008) defined that also the irradiance plays its role into the activation. By increasing the light-irradiance intensity (E) (energy per unit of area and by the photon flux on the surface of the catalyst material) the reaction rate will raise, since more protons are diffused.

**Humidity**

Since the TiO$_2$ surface carries molecular water (both weakly and strongly bonded) and hydroxyl groups, the quantity of water vapor could influence the photo-catalytic reaction. A low presence of water vapor retards the photo-catalytic degradation, and impedes the total mineralization of CO$_2$, as final product. However, an excessive amount of water vapor will cause the reduction in the reaction rate, since water molecules can occupy active sites of the TiO$_2$ surface (Zhao and Yang, 2003). Therefore, the influence rate of water vapor in the photo-catalytic reaction changes according to the contaminants features. It is known that the substrate of the photocatalyst plays an important role. Ao and Lee (2003) reported an almost constant NO conversion with the increase of the relative humidity from 10% until 70% using Teflon. Devahasdin et al., (2003) reported an increased NO conversion in the range of 0-50% relative humidity and afterwards becomes constant using pyrex as substrate. Wang et al., (2007) reported a steady increase of the NO conversion with an increase of the relative humidity from 8% to 100% using a woven glass fabric as substrate. Finally, Yu and Brouwers (2009) found an increase of the NO conversion from 10 to 30% when increasing the relative humidity from 30-70% which are in line with the results of (Wang et al., 2007). In outdoor applications, the uptake and release of moisture by wood can result beneficial for the NO conversion since it will release moisture when relative humidity is decreasing.

**Flow rate**

The flow rate is the amount of air flowing per unit of time. It can vary under practical condition, as it depends on the wind speed but also on its direction. It is connected with the residence time of the pollutants on the active surface of the material (Hunger and Brouwers, 2008). In particular, a high flow rate decreases the residence time on the photo-catalytic surface leading to a lower NOx degradation per unit of time. On the other hand a low flow rate allows a longer permanence of the pollutants on the PCO particles, enhancing the performances of the coating.

**Contaminant concentration**

A different reaction rate is shown during the photo-catalytic process, depending on the contaminants amount. Obee and Brown, (1995) describe the dependence between contaminants inlet and reaction rate. For low contaminant concentration, less than 1 ppm,
the degradation of formaldehyde is higher than the acetaldehyde one, because of the higher adsorption strength of the former on the catalyst surface. These data suggest that the reaction rate was based on the adsorption of contaminants in the TiO\textsubscript{2} surface, as the reaction kinetics was mass-transfer limited in the low concentration region (Zhao and Yang, 2003).

**Support material**

The substrates where TiO\textsubscript{2} is deposed on plays a crucial role that influences the efficiency of the reaction (Ângelo et al., 2013). Parameters like: a) chemical composition of the substrate; b) surface roughness and surface structure of the substrate, strongly influence the mass transfer. Regarding the mass transfer, Zhang et al. (2013) analyzed the influence of the viscous layer along the board surface and concluded that its behavior is strictly connected to the surface roughness. The artificial roughness created in the study increases the turbulence intensity, resulting in an increased mass transfer, and thus in an improved degradation rate of the photo-catalysis. However, too high values of relative roughness could reduce the photo-catalytic efficiency, because reattachment of the free shear layer might not occur and the rate of heat transfer enhancement will not be proportional to that of friction factor (Ebrahim et al., 2002). Therefore in this study, different support materials will be analyzed by changing its chemical composition (e.g. magnesium binder and cement binder) and its surface roughness (i.e. 1.0, 1.5, 2.0 and 3.0 mm width wood wool strands).

### 5.4.3 Overview of the performed test

The WWCB used in this study are commercially produced by Knauf Insulation by using spruce wood wool, covered by a binder. The binder used for the manufacture of these boards is consisting of W (CEM I 52.5 R White) and limestone powder, termed CEM WL. The four WWCB used in this study are made of different types of wood wool strand widths, namely 1.0, 1.5, 2.0 and 3.0 mm in width termed C-n, where n is indicating the width of the strands in mm. Besides the cement binder also a magnesium binder (C3M) and a board of CEM I 52.5R (C3G) both with wood wool strand widths of 3.0 mm were tested to observe the behavior of the substrate. In line with the previous tests the influence of the binder type on a flat WWCB surface is studied on the samples C1.5 now made of magnesium (C1.5MF1) and compared to C1.5 made with CEM I 52.5R White and limestone powder (C1.5KF1). The hypothesis is that the flat board, produced in the laboratory by using the board recipe of the company and applying high pressure (to densify the matrix), the boards should have a much lower performance. Table 5.1 briefs the support materials with their main characteristics. Using a Keyence VHX 5000 microscope, the profiles of the samples in depth and 3D indications of the surface roughness (SR) are obtained as illustrated in Figure 5.5 of which part of this results are published elsewhere (Gauvin et al., 2018). Dissecting each board (200 x 100 mm\textsuperscript{2}) in three parts with an area of 50 x 50 mm\textsuperscript{2} the average specific surface area is calculated. This by defining three horizontal and three vertical cross sections per segment with a length of 48 mm. The depth profile is then obtained by averaging an area surrounding the profile of 10 mm\textsuperscript{2}, at 0.5 mm intervals determining the maximum and minimum height of each profile. The depth profile is used as an indicator for the SR in which for instance C1
can be classified as having a low SR (avg. depth 2.63 mm) and C3 a high roughness (avg. depth 7.71 mm).

**Table 5.1:** Chemical and physical composition of tested supports.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Board thickness [cm]</th>
<th>Board strand width [mm]</th>
<th>Density [kg/m³]</th>
<th>Porosity [%]</th>
<th>Specific surface area [mm²]</th>
<th>Avg. depth [mm]</th>
<th>Binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1.5</td>
<td>1</td>
<td>450</td>
<td>79.05</td>
<td>2474</td>
<td>3.02</td>
<td>W+LP</td>
</tr>
<tr>
<td>C1.5</td>
<td>2.5</td>
<td>1.5</td>
<td>464</td>
<td>83.07</td>
<td>2795</td>
<td>5.89</td>
<td>W+LP</td>
</tr>
<tr>
<td>C2</td>
<td>2.5</td>
<td>2</td>
<td>448</td>
<td>83.24</td>
<td>2595</td>
<td>4.25</td>
<td>W+LP</td>
</tr>
<tr>
<td>C3</td>
<td>2.5</td>
<td>3</td>
<td>453</td>
<td>82.5</td>
<td>3265</td>
<td>10.47</td>
<td>W+LP</td>
</tr>
</tbody>
</table>

Evaluated samples do determine the influence of binders

| C3G    | 2.5                   | 3                        | -               | -           | -                           | -              | CEM I 52.5 R |
| C3M    | 2.5                   | 3                        | -               | -           | -                           | -              | Magnesia    |
| C1.5M  | 2.5                   | 1.5                      | -               | -           | -                           | -              | Magnesia    |

Evaluated influence of binder and flatness of the board

| C1.5MF1| 0.8                   | 1.5                      | -               | -           | -                           | -              | Magnesia    |
| C1.5KF1| 0.8                   | 1.5                      | -               | -           | -                           | -              | W+LP        |

The profiles reveal a proportionality between strand width of the board and its average maximum depth, indicated on the profiles. The board with 1.5 mm and 2.5 mm strands are not very different in the tested samples. However, in general the increasing width of the wood wool results in a more open structure, leading to the formation of deep cavities varying between 3 and 10 mm. The presence of these cavities and unevenness of the surface results in a larger specific surface area of the WWCB available for the photocatalytic coating.

**Assessment durability**

In order to test the influence of the substrate, the experiments are carried out on various conditions listed in Table 5.2. Static and dynamic washing is performed for 2 h on the C1.5 boards. For the static treatment, the samples (SW2) were submerged under water (1.5 l). The water level was kept at 3 cm (twice the height of the board) without any further water movement. For the dynamic water treatment the samples (DW2) were submerged under water and the chamber was set in motion by a Stuart reciprocating shaker SSL2 with a rotating speed of 250 rpm, creating extreme conditions to evaluate the bond of the TiO₂ on the WWCB. This was even further evaluated by a 24 h shaking period (DW24).

**Table 5.2:** Test specimens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2</td>
<td>SW2</td>
<td>Static washed for 2h</td>
</tr>
<tr>
<td>C2</td>
<td>DW2</td>
<td>Dynamic washed for 2h</td>
</tr>
<tr>
<td>C2</td>
<td>DW 24</td>
<td>Dynamic washed for 24h</td>
</tr>
</tbody>
</table>
Figure 5.5: (a) Visual comparison among tested tiles analyzed by Keyence microscope. The color change from red to dark blue displays the increasing the depth; (b) Average profiles of a board with C1, 1.0 mm; C1.5, 1.5 mm (Gauvin et al., 2018); C2, 2.0 mm; C3, 3.0 mm strand widths.
### 5.4.4 PCO experiment

**Coating the WWCB with a PCO solution**

The photo-catalytic solution used as coating is an aqueous suspension with photo-catalyst concentration of 40%, stabilized in water. The samples for photo-catalytic oxidation tests were prepared by coating an aqueous suspension of the photo-catalyst on boards with dimensions of 20 x 10 cm$^2$. The PCO dosage for all the samples is 2 mg/cm$^3$, thus 0.4 g per board, being the geometric area 200 cm$^2$. A further dilution in 8 g of water has been applied to ensure a uniform distribution of the coating on the support surface (dry coating).

The solution has been distributed on the board by brushing. An evaluation of the amount of PCO left in the brush has been performed by cleaning the brush and measuring the left over amount after evaporation. The amount of unapplied PCO is found to be limited to the 3-5% of the total coating mass. After the coating, boards are left in a ventilated oven at 70°C, in order to remove the water from the suspension. From each board type three samples were prepared.

**PCO test procedure and experiment**

The laboratory test set-up for carrying out the photo-catalytic oxidation of nitric oxide is designed according to standard ISO 22197-1:2007. The setup consists of four parts, namely reactor cell, light source, a gas supply, and chemiluminescence NOx analyzer. The setup of the machine is schematically illustrated in Figure 5.6.

![Diagram of photo-catalytic degradation set-up](image)

**Figure 5.6:** Diagram of photo-catalytic degradation set-up. 1) NO gas supply 2) NO$_2$ gas supply 3) Synthetic air supply 4) Mass controller meter 5) Humidifier 6) Humidity controller 7) Temperature and relative humidity sensor 8) Valve 9) Light source 11) Reactor 12) NOx analyzer 13) Computer 14) Vent (Yu and Brouwers, 2013).

NO gas was used as the target pollutant, consisting of 50 ppm NO stabilized in N$_2$. The final NOx concentration was diluted to 1ppm using air which was composed of 20.5 vol% of O$_2$ and 79.5 vol% of N$_2$. By activating the sample coated by TiO$_2$ with visible light and monitoring the NOx concentration, the reduction of NOx in time is measured. The visible light intensity is set at 10.87 W/m$^2$. It has been measured by VIS-BG.
radiometer measuring a wavelength of 400-600 mm with maximum relative sensitivity of 460 mm. The experiment takes place at defined temperature and relative humidity, respectively 24.6 °C and 50% RH. The duration of each test is 30 minutes. Since the room conditions could vary, all the samples are tested using three different airflow rate. The air flow is realized by pressure differences. In the Scenario 1 the air flow is 3 l/min, Scenario 2 the air flow 2 l/min, while in the Scenario 3 it is 1 l/min. Table 5.3 presents the amount of synthetic air and NOx for each scenario.

Table 5.3: Flow rate scenarios.

<table>
<thead>
<tr>
<th>Air flow speed [l/min]</th>
<th>NO concentration [ppm]</th>
<th>Air [l/min]</th>
<th>NO [l/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario 1 3</td>
<td>1</td>
<td>2.94</td>
<td>0.06</td>
</tr>
<tr>
<td>Scenario 2 2</td>
<td>1</td>
<td>1.96</td>
<td>0.04</td>
</tr>
<tr>
<td>Scenario 3 1</td>
<td>1</td>
<td>0.98</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The study concerning the estimation of the flow behavior in proximity of the wood wool has been performed by using CFD (Computational Fluid Dynamics) code ANSYS Fluent 15. The 3D domain has the following dimensions X (length), Y (height), Z (width) = 50 x 7.5 x 25 mm³, while the dimensions of the wood wool strands are width x height = 2.4 x 0.9 mm². The strands are oriented at 45 or 90 degree angle, to represent the random structure of the strands. Velocity inlet is applied on the left side of the domain, with constant uniform velocity of 0.16 m/s, and turbulent intensity of 5%. Pressure outlet is applied to the right side of the domain, with zero pressure gradient, so that it allows the passage of the flow without acceleration or deceleration. Symmetry boundary condition is applied to the sides of the domain (in Z-direction) in order to limit the computational demand and still correctly describe the flow along the wood wool board. The top of the domain is modelled as a wall.

5.5 Influential factor analysis

5.5.1 Introduction

The enhancing performance of the coating, which is surface related, could depend on many factors like wider surface area, porous microstructure, surface roughness and water desorption and adsorption isotherms that will be discussed in detail in this paragraph.

Wider surface area: Due to the porous structure of the WWCB, the coated surface area exposed to the flow is higher. Therefore, the reacting surface is wider, resulting in an increasing amount of degraded pollutants.

Porous structure: The hierarchical porous structure of the WWCB is beneficial for the dispersion of TiO₂ because it creates larger catalytic area (Wang et al., 2014a). The gas diffusion could also be improved, because the WWCB has more cavities available. Furthermore, the porous structure could stimulate the deep activation of the substrate, as it allows the passage of the light till deep layers of the board, instead of only the surface layer (Wang et al., 2014a).
**Roughness of the surface**: Zhang et al. (2013) analyzed the influence of the surface roughness on the fluid flow, and the mass transfer associated to different type of flow, finding a strict relation between them. In case of photocatalyst smooth surface, the air flow forms a laminar sub-layer close to the surface, impeding the mass transfer of reactants to the PCO coating. The artificial roughness increases the turbulence intensity, resulting in an increased mass transfer, and thus in an improved degradation rate of the photo-catalysis. Hence, a rough surface could increase the formation of turbulent flow, and facilitate this process.

### 5.5.2 Analysis of the NO degradation

**Effect of the flow rate and strand width**

Figure 5.7 illustrates the NOx removal results of the evaluated boards, under the same operating conditions, applying three different flow speeds. Firstly, the C2 and C1.5 have the best performance reaching the 97% of NOx removal at a flow of 1 l/min. Although C1 board types are not able to perform such high degradation, its degradation rate of pollutants has only minimum values around 80%. As already mentioned by Hunger and Brouwers (2008) there is a proportionality between the degradation rate and the air flow speed.

![Figure 5.7: Degradation rate of NOx using PCO coating on WWCBs boards using air flows of 1, 2 and 3 L/min.](image)

A low air flow speed corresponds to a high degradation rate, since it causes the increasing of the residence time of the NOx particles on the substrate (Yu and Brouwers, 2009). As consequence, the pollutants absorption at the catalyst surface increases. The absorbed molecules have more possibilities to be activated in the reaction and be oxidized (Zhong et al., 2013). This type of flow is representing an indoor situation near a wall construction. However, the air velocity inside a building is the most difficult parameter to measure accurately. The slow rates of air movements (between 0.1 and 2.0 m/s), the high variability and the presence of gusting and lulls could cause variation in the observed velocity (Heerwagen, 1996).
It is observed from Figure 5.7 that the C3 degradation results are the lowest, even if the strand width and SA are both the highest among the boards. Note that no NO₂ as an intermediate product is observed during the measurements. These products can form in case no further adsorption occurs from the surface of the sample to air (Yu et al., 2010).

To the authors knowledge there are no studies revealing such high degradation while using such a low quantity of photo-catalyst. An additional study is performed with long time measurements of 12h revealing a constant degradation of 100% for the 1.5mm board.

![Graph](image)

**Figure 5.8:** Degradation rate of NOx using PCO coating on flat WWCBs.

The presence of flat surface leads to a lower surface area (SA) available for the distribution of the coating, and thus a decrease of the degradation rate. Compared with rough boards, a reduction of degradation of 60% or higher, in both KF1 and MF1 can be observed.

From the results obtained, it is evident that the different binder applied plays a role on the degradation rate. The presence of PC as binder provides a higher degradation rate compared to magnesia cement. In general, the difference in performance increases with the reduction of air flow speed, as in the case of the rough boards. However, the KF1 seems to be less affected by the flow speed, showing a degradation between 45 and 35%. Pilarska et al., (2013), indicates a negative surface charge for unmodified magnesium hydroxide with a pH >10 (pH magnesia board 10.2). Furthermore, the surface charge of the TiO₂ suspension is also negatively charged (ζ = -33), indicating possible repulsion and reduced adhesion which lowers the performance of this binder.

As can be observed from Figure 5.7 and Figure 5.8, the substrate (1.0-3.0 mm) has a remarkable effect on the photo-catalytic performance. The photo-catalytic coating is based on a reaction taking place on the surface of the photo-catalytic material distributed on the substrate surface. Due to its roughness, three main phenomena affect the boards’ performances.
1) Contrary to a smooth surface, WWCB provides an enhanced exposed surface area for the PCO distribution, increasing the spread of the TiO$_2$ particles on the surface.

2) The high surface area and the interconnected pore structure allow to pass through a high volume of pollutant air and to realize (because of acting obstacles) a high mass transfer (tested airflow resistivity is 13-15 KNs/m$^4$ according to ISO 9053, attributed to the high porosity of $\pm$ 80%).

3) The surface roughness influences the flow around the board, creating a non-uniform laminar boundary layer. Surface roughness or small protuberances on the structure might influence the flow in proximity of the board. Hence, the narrow region close to a surface (so called viscous sub-layer) could be easily modified by small roughness elements, affecting then the entire flow (Munson, 2005). Figure 5.9 illustrates how the flow behaves corresponding to a turbulent and laminar boundary layer.

![Figure 5.9: Influence of the surface roughness on the viscous boundary layer (Munson, 2005).](image)

Since the NOx molecules have a molecular mass and dimension similar to the air, their exact trajectory inside the turbulent flow is not easy to model. However, physical approximation of this behavior has been developed. Vol et al., (1992) provided a model of the particles-wall collision, taking into account also the small dimension particles and the influence given by the roughness of a surface. The estimation of the behavior of the flow in proximity of a wall a geometric representation of the WWCB structure has been simulated by using CFD software as presented in Figure 5.10.

Because of the open structure of the board air is moving through it carrying NOx particles. The open structure and cavities of the WWCB host a greater and more homogeneous distribution of the coating, increasing the surface available for the reaction. In spite of the reduced flow speed in proximity of the wall, the flow through the matrix is further slowed down, increasing the residence time and enhancing the degradation rate.
Many studies state the improvement of the photo-catalytic activity with the increment of the surface area of the support (Ramirez et al., 2010; Wang et al., 2014). However, the SA and the support roughness of WWCB are, together with the NOx degradation, only partially proportionally dependent as indicated in Figure 5.11.

Considering PC as a binder, the increment of roughness within certain values (from 2 to 5 mm) results in a higher degradation percentage (> 90%). Despite of the greater SA and roughness, the NOx degradation rate for C3 results 40% lower than C2. Hence, for WWCB, the growth of the SA is not positive if it overcomes specific values of roughness. A possible explanation is that a rough surface has more shadows, due to its heterogeneous conformation, and thus it receives less protons (Zhang et al., 2013). This would lead to a lower activation of the photo-catalytic coating, as well as the impossibility for visible light to reach the deepest layers of the board. However, a more likely explanation is related to the airflow rate, which is significantly reduced close to the...
deepest layers reducing the amount of available pollutants to degrade and is also observed in the created model presented in Figure 5.10.

Effect of the binder (support)

![Figure 5.12: NOx degradation for supports with different chemical composition and air flow speed.](image)

The influence of the support is clearly illustrated in Figure 5.12. While only the chemical composition and with that the color appearance is changed, the performance of the boards are significantly altered. C3 presented in Figure 5.11 has an average degradation of 58%, 41% and 31% for a flow speed of 1, 2 and 3 respectively. C3G, clearly illustrates a similar performance compared to C3 but its performance lays slightly higher especially in the high region flow rate. Furthermore, C3M performance under similar conditions lower due to the low adherence of TiO₂ particles on the substrate and is in line with the results of the flat boards.

5.5.3 Durability

Especially in case of outdoor applications, the photo-catalytic coating has to ensure the adhesion to the surface also in presence of rain (Sopyan et al., 2011). Many techniques are developed in order to ensure the stability of the coating on the substrate (Mendoza et al., 2014). In this case the distribution of the coating on the WWCB has not been applied following any of these methods to increase the immobilization of the catalyst particles on the substrate. Figure 5.13 displays the NOx degradation rate after static and dynamic washing of C2 samples. After 2h washing (both static and dynamic) the degradation performance is reduced by ± 30% (1 l/min) and with the enhancement of the air flow speed (3 l/min) reduces by ± 45%. The 24h dynamic washing affects more the degradation due to the removal of the photo-catalyst. Despite this, the board is still able to guarantee a degradation of 26.6%, since part of the coating is still present.
Since particles are removed after 24h washing it is believed that there is no chemical bond and that the adhesion is related to the surface charge of the substrate and TiO$_2$ which allows them to adhere onto each other (Sopyan et al., 2011). Finally, the porous structure of the WWCB could limit the migration of particles from the support. This because the open structure allows a deep penetration of the TiO$_2$ into the material (Rachel et al., 2002).

An estimation of the amount of coating left after the dynamic washing of 2 h can be done by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX). This surface analytical technique is able to give a qualitative information concerning the compounds on the surface analyzed by using analysis of characteristic X-rays (EDX or EDS analysis). Figure 5.14 displays the presence of photo-catalytic coating on both washed and unwashed wood wool strands, after photo-catalytic application by dry coating.

**Figure 5.13:** NOx degradation rate of C2 samples after 2h static (SW) and 2 and 24h dynamic washing (DW) measured with airflow speeds.

(a) (b)
Figure 5.14: (a) SEM picture of a wood wool strands at a magnitude of 50 um coated by photo-catalytic material; (b) EDX pictures of the same coated wood wool strand spot; (c) SEM picture of a wood wool strands at a magnitude of 50 um coated by photo-catalytic material and dynamically washed for 2h; (d) EDX pictures of the same dynamically washed wood wool strand spot.

Although the amount of photo-catalytic material is reduced after the washing treatment, the presence of TiO$_2$ particles is visible. The distribution results less homogeneous in the case (b) (after washing), thus the coat efficiency will be also reduced, due to the lower surface area covered. However, since particles are almost completely removed after 24h washing (degradation around 15%) it is believed that there is no chemical bond and that the adhesion is related to the surface charge of the substrate and TiO$_2$ which allows them to adhere one to each other (Sopyan et al., 2011). On the other hand the wood could work as an absorptive element which withholds the TiO$_2$ particles in its structure.

Finally, the porous structure of the WWCB could limit the migration of particles from the support. This because the open structure allows a deep penetration of the TiO$_2$ into the material (Rachel et al., 2002).

5.6 Conclusions

- This study shows the suitability of WWCB as an air purifying material, besides thermal insulating, sound absorbing and fire reducing properties, and adding by that an additional feature to the product. WWCBs have good support properties that allow the use of very low quantity of TiO$_2$, while realizing a high degradation rate (> 95%) increasing not only the indoor air quality but also making the application of TiO$_2$ for air purification cost efficient. The reduction in the coating amount reduces the cost of the coating, providing an improved performance for lower price. The decreasing use of energy for ventilation minimizes the costs connected to the indoor air purifying, enhancing its independence from energy sources. This extraordinary performance is related to the high surface area while maintaining a high mass transfer due to the open surface structure. The TiO$_2$ particles are homogeneously spread on a wider surface, allowing a greater activation of the compound, and thus higher degradation amount. Moreover, any additional compounds (NO$_2$) are produced from the degradation of NOx. From the study it also can be concluded that:
• A higher surface area does not necessarily indicate a higher degradation rate, but is also strongly related to the surface roughness that influences the mass transfer between the pollutants and the active surface.

• The presence of porosity with depth higher than 4 mm is not able to rise the coating performance.

• It is revealed with a water treatment that adhesion between the support and the coating is not chemically bound. However, by dynamic washing, the TiO₂ particles are not completely washed out.

• The reduction in the photo-catalytic amount does not nullify the degradation, and it shows a possible relation with the type of binder used.

• The PC provides the best adhesion of the coating on the board, although the coating loses efficiency if applied in early stages of board manufacture.
Chapter 6

Modeling and optimization of the sound absorption of wood wool cement boards


6.1 Introduction

In order to avoid high noise levels or improve speech intelligibility, porous materials and green walls (Alessandro et al., 2015) are applied frequently in the built environment. A popular type of porous material is mineral wool (Oliva and Hongisto, 2013), characterised by a high porosity in the range of 92-98% and by a flow resistivity of 5-30 kNs/m$^4$ (Wang and Torng, 2001). In recent years, the interest in the use of natural resources in sound absorbing materials is growing for instance by applying spruce wood wool strands, hemp particles, straw, flax and coconut fibres and reeds (Glé et al., 2012; Botterman et al., 2016; Oldham et al., 2011; Asdrubali et al., 2015). This is attributed to their low density, high availability (Zabel & Morrell, 2012; Sjöström, 1993), possessing no adverse health effects (Berardi & Iannace, 2017) and low ecological footprint (Berardi & Iannace, 2015; Asdrubali et al., 2015). The use of natural strands, however, can be traced to one century ago. Around 1920, after the invention of Portland cement, wood wool cement boards (WWCB) were developed (van Elten, 2006), possessing favourable mechanical, thermal and acoustical properties (Glé et al., 2011; Doudart de la Grée et al., 2014b; Burd, 1984; Berardi & Iannace, 2015). Moreover, due to the mineralisation of the wood wool by the cement, the boards possesses fire resistant properties and resistance to biodegradation (van Elten 2006), hence, become more durable. Nowadays, this material is still widely applied, mostly as an acoustical ceiling e.g. in gyms, school buildings, parking garages but also utilized in sound barriers. Annually 16 million square meters of boards are produced (van Elten, 2015). To lower the environmental footprint of the boards, part of the cement can be replaced by limestone powder or industrial by-products up to 36% (Doudart de la Grée et al., 2015). Currently, research is successfully conducted to further reduce the use of cement (Doudart de la Grée et al., 2014a; Doudart de la Grée et al., 2014b).

Generally WWCBs are characterised by a porosity in the range of 70-85% (Doudart de la Grée et al., 2014b; Botterman et al., 2016) and a flow resistivity of 1.7-8.5 kNs/m$^4$ (Botterman et al., 2016), having sound absorbing properties which have not been reported yet. In contrast to mineral wool, the WWCB properties are inhomogeneous. This is due to the randomly distributed natural wood wool strands with varied dimensions, which are covered by a thin layer of binder varying in thickness between 80-400 µm (Doudart de la Grée, 2014a). Although widely applied, no systematic study on the acoustical properties
on WWCBs has been reported. In the present study (visualised in Figure 6.1), a systematic investigation is carried out by making use of acoustic impedance models. The sound absorbing properties are studied for different design parameters of the WWCB as density and strand size. The suitability of an impedance model depends on the morphology of the used material and the number of input parameters consequently depends on complexity of the microstructure. Previous studies (Glé et al., 2011; Wassilieff, 1996) reported good agreements between simulations and experiments of wood based porous materials. Various models such as the Attenborough model (Attenborough, 1983) and a combination of the Johnson et al. model (Johnson et al., 1987) and Zwicker and Kosten model (Zwicker & Kosten, 1949), are used depending on the type of wood-based material (Wassilieff, 1996; Glé et al., 2012; Berardi & Iannace, 2015). Whereas the boards investigated in the mentioned studies consist of densely packed particle shaves, loosely packed long wood strands (± 25 mm) are used for producing WWCBs, making the WWCBs different (density <550 kg/m^3) and more inhomogeneous compared to high density boards with natural fibers. Besides the WWCB material properties that influence the sound absorption, WWCBs are often mounted directly against the floor/ceiling construction while implementation of a certain air cavity can lead to a significant improvement of the sound absorption and will provide valuable contribution on the speech intelligibility (Kang & Fuchs, 1999).

![Figure 6.1: Schematic overview of the current study, with the dashed lines indicating visualizations and sub sections.](image-url)
6.2 Materials and Experimental methodologies

6.2.1 Density and wood to binder characterisation of WWCB
Three commercial WWCBs (supplied by Knauf Insulation), using a thickness of 25 mm, with different strand widths (1.0, 1.5 and 2.0 mm), where investigated in this study. Attributed to the difference in strand width, the 1.0 mm strand width WWCB has a higher total strand surface area compared to the 1.5 and 2.0 mm, hence, more binder material (+18%) is needed to manufacture this type of board. The bulk density was determined by measuring the mass of the sample and dividing it by the bulk volume of the sample for a large number of samples (±25) per board.

The differences in board density are not only based on a fluctuating amount of material present in the samples, but is also related to the actual wood-to-binder ratio. Therefore, the wood and binder amount is determined as described in (Quiroga and Rintoul, 2015).

6.2.2 Acoustic impedance measurement
Surface impedance measurements were performed with the purpose to validate the used impedance models and predict the unknown input parameters. The surface impedance measurements were conducted by making use of a six-microphone impedance tube with an inner diameter of 40 mm. From on the obtained surface impedances, the normal incidence sound absorption of the samples was determined. With a cut-off frequency of 5022 Hz, it was found that until the 2800 Hz the impedance tube shows a rather low deviation (<5%) in the absorption coefficient when running an empty tube. The normal incidence sound absorption average (SAA-value) according to ASTM C423 (ASTM, 2014) calculation method is used in this study to describe and optimize the single value sound absorption. This value represents the average normal incidence sound absorption value over the 200-2500 Hz 1/3 octave bands.

6.2.3 Impedance models and their input parameters
Since the evaluated frequency range (177-2828 Hz) is much larger than the phase decoupling frequency (1-2 Hz) of the WWCB, the board is unable to support elastic wave propagation and can be considered as a rigid frame for this range. Therefore, the following rigid-frame impedance models were considered in this study with the number of input parameters of these models in parenthesis: Attenborough model (4), Johnson-Champoux-Allard (JCA) model (5) and Johnson-Champoux-Allard-Lafarge (JCAL) model (6) (Champoux and Allard, 1991; Attenborough, 1983; Johnson et al., 1987; Lafarge et al., 1997). For all these models, the parameters open porosity and flow resistivity were measured. The other unknown parameters namely tortuosity, shape factor, viscous characteristic length, thermal characteristic length and static thermal permeability (when applicable) were determined by making use of an inverse calculation method (Atalla and Panneton, 2005) based on the obtained acoustic impedance measurements. However, both Wasselief (1996) and Glé et al. (2012) found deviations between the modelled and measured sound absorption of wood based materials when porosity as measured using a pycnometer was used in the impedance model. Therefore, in this study the porosity was initially determined by the inverse calculation method and named the acoustic effective
porosity. Later (after an appropriate model was selected) the suitability of utilizing the measured porosity instead of the acoustic effective porosity was evaluated.

*Open porosity*

The open porosity is calculated by the ratio between the skeleton volume and the bulk volume that is measured by using a helium Pycnometer using a sample size diameter of 46 mm measured by using a calliper.

*Flow resistivity*

The flow resistivity \( \sigma \) [Ns/m\(^4\)] was measured by sending an air flow with a constant velocity through the WWCB-samples to measure the air velocity and pressure drop through the sample. The geometry of the WWCB-sample was cylindrical (diameter of 97 mm and a thickness of 25 mm). The pressure difference between the two faces of the samples was measured with a differential manometer connected to multi-meters; the volumetric flow rate was measured with a flow meter. The flow resistivity is calculated according to ISO 9053 using:

\[
\sigma = \frac{\Delta P}{Q \times \pi \times r^2 \times d}
\]  

(6.1)

where \( \sigma \) is the flow resistivity [Ns/m\(^4\)], \( \Delta P \) is the air pressure difference across the test specimen with respect to the atmosphere [Pa], \( Q \) is the volumetric airflow rate passing through the sample [m\(^3\)/s], \( r \) is the sample radius [m] and \( d \) is the thickness of the sample [m].

*Unknown parameters and parameter relations*

To obtain the unknown parameters of the impedance models, the non-linear least square method in the curve fitting toolbox in Matlab (R2014b) was used. With this algorithm, parameter values for the applied impedance model were sought that give the best fit to the measured normal incidence sound absorption in the range of 200-2500 Hz. This fitting technique has already been successfully used to study the sound absorption of a porous media (Johnson et al., 1987; Olney and Panneton, 2008; Atalla and Panneton, 2005). Afterwards, relations between density and the fitted data of the parameters derived from the plotted regression trends (linear, exponential and power) were determined. Based on the found relations the root mean square deviation values (RMSD) were used to determine the best fit.

6.3 Measured parameters and choice of impedance model

6.3.1 Density and wood to binder properties

The bulk density results in Figure 6.2a show that the range in densities over the samples is very large, which means that the WWCBs are highly inhomogeneous.
From the results in Figure 6.2b, it can be concluded that because of the higher binder amount, the WWCB using 1.0 mm strand width have a lower wood-to-binder ratio compared to 1.5 and 2.0 mm strands width. Although the 1.5 and 2.0 mm strands width WWCBs have a similar wood-to-binder ratio the 2.0 mm shows a larger spread of values compared to the 1.5 mm.

![Figure 6.2: Boxplot of (a) Bulk density; (b) The wood-to-binder ratios of the WWCB versus the wood wool strand width.](Image)

### 6.3.2 Choice of impedance model

To select the appropriate impedance model for WWCB, a 25 mm thick WWCB, with a 1.0 mm strand width and a density of 448 kg/m³ was evaluated. All parameters from the previously mentioned impedance models where fitted on the measured acoustic impedance with exception of the flow resistivity which was measured for the evaluated sample. For the fitted parameters, the initial, lower and upper value limits for the fitting process are listed in Table 6.1.

![Table 6.1: Input parameters for the curve fitting of the studied impedance models.](Image)
The obtained input parameter values for the JCAL-model within the described parameter range (Table 6.1) were found to alter when changing the ranges. This means that no unique values were found, which is caused by the larger amount of unknown input parameters. Hence, the JCAL-model was not further considered. The Attenborough and JCA models gave unique results and are therefore considered. They take into account the complex internal pore structure of the WWCB, by incorporating besides the flow resistivity, porosity and tortuosity either a pore shape factor or making use of viscous and thermal characteristic lengths, hence, are able to fit the measured values as presented in Figure 6.3.

**Figure 6.3:** Fitted values by the Attenborough and JCA models compared to the measured values for (a) Normal incidence sound absorption; (b) Real and imaginary values of the normalized surface impedance. Results apply to a 25 mm thick WWCB (1.0 mm strand width and density of 448 kg/m$^3$).

It needs to be noted that the absolute deviations for the whole frequency range are low (see Figure 6.3), which indicate that both Attenborough and the JCA-model provide very accurate predictions. Hence, these models are further studied to select a single model to predict the WWCB sound absorption. Ten samples with a 1.0, 1.5 and 2.0 mm strand width and varying densities were evaluated by calculating the relative deviation $\varepsilon_j$ between the predicted and measured values for the 1/3 octave bands in the frequency range 200-2500 Hz as:

$$\varepsilon_j = \frac{\alpha_{\text{model},j} - \alpha_{\text{measured},j}}{\alpha_{\text{measured},j}}$$  \hspace{1cm} (6.2)

with $\alpha_{\text{model},j}$ the absorption coefficient of 1/3 octave band $j$, as obtained from the fitted impedance model, by using either the Attenborough or the JCA model. The results are presented in Figure 6.4.
From the results presented in Figure 6.4 with the bars indicating different samples with varying densities, it can be seen that for both models $\varepsilon_j$ was close to zero above 1000 Hz, but increases below the 1000 Hz. This behaviour can be explained by the low sound absorption values in the low frequency region as illustrated in Figure 6.3a which leads to large relative errors. The errors seem to be high, but it needs to be noted it is about relative errors (i.e. if the absorption value for the 200 Hz 1/3 octave band is 0.01 and the predicted value is rounded of to 0.02, the error will be 100%). Based on the results, it is concluded that the deviation of the measured normal incidence sound absorption for the JCA-model was, especially for the lower frequencies, lower than that from the Attenborough model. The Attenborough model has a lower amount of input parameters which could be the reason of this larger deviation. Therefore, the JCA model is for modelling the sound absorption of the WWCB chosen.

### 6.3.3 Johnson-Champoux-Allard (JCA) model

The JCA-model (Johnson et al., 1987; Champoux and Allard, 1991) involves five physical parameters: the open porosity, flow resistivity, tortuosity and the viscous and thermal characteristic lengths. Based on these input parameters, the effective density as:

$$\rho_{e}(\omega) = \frac{\alpha_{\infty} \rho_0}{\phi} \left(1 + \frac{\alpha \phi}{i \omega \rho_0 \alpha_{\infty}} \left[1 + \frac{4i \alpha_{\infty} \eta \rho_0 \omega}{\sigma^2 \Lambda^2 \phi^2} \right]\right).$$

(6.3)
and the viscous effects, and the effective bulk modulus as, describing the thermal effects, are calculated as:

\[ K_e(\omega) = \frac{\gamma P_0}{\phi} \left( \gamma - (\gamma - 1) \left( 1 + \frac{8\eta}{i\Lambda^2 N_{pr} \omega \rho_0} \sqrt{1 + \frac{i\rho_0 \omega N_{pr} \Lambda^2}{16\eta}} \right)^{-1} \right)^{-1}, \]  

(6.4)

with \( \alpha \) the tortuosity [-], \( \rho_0 \) the density of air [kg/m\(^3\)], \( \phi \) the porosity [-], \( \sigma \) the flow resistivity [Ns/m\(^4\)], \( \omega \) the angular frequency [1/s], \( \eta \) the viscosity of air (\( \approx 1.84 \times 10^{-5} \)) [-], \( \Lambda \) the viscous characteristic length [\( \mu m \)], \( \gamma \) ratio of the specific heat capacity (\( \approx 1.4 \)), \( P_0 \) the atmospheric pressure (\( \approx 101,320 \) Pa), \( \Lambda' \) the thermal characteristic length [\( \mu m \)] and \( N_{pr} \) the Prandtl number (\( \approx 1.4 \)) [-].

Based on these equations, the characteristic impedance \( Z_c = \sqrt{K_e(\omega) \cdot \rho_c(\omega)} \) and the wavenumber \( k = \omega \sqrt{\rho_c/K_e} \) are determined. From these parameters, the surface impedance \( Z_s = -jZ_c \cot(kd) \) is defined implementing the board thickness \( d \). Finally the normal incidence sound absorption is calculated \( \alpha = 1 - \left( \frac{Z_s - \rho_0 c}{Z_s + \rho_0 c} \right)^2 \) with \( \rho_0 c \) representing the impedance of air [Pa·s/m].

### 6.3.4 Open porosity

The measured porosities according to Section 6.2.3 are presented in Figure 6.5. The results show that the porosity values for boards having different strand widths are in the same order of magnitude and independent of their varying wood to binder ratios. This can be explained by (1) the low solid volume present in the sample (i.e. 20% at 450 kg/m\(^3\)) and (2) the total binder volume and skeleton volume of the wood are not very different.

To evaluate the influence of the open porosity, different values were adopted in the model while keeping the other input parameters constant. From the results, it was found that when using one of the measured porosity values (79%) as an input parameter for the impedance model no proper fit at around the 2000 Hz peak was obtained what negatively influences the accuracy of the prediction. As previously discussed, both Wassilieff (1996) and Glé et al. (2012) obtained similar deviations and as an explanation indicated that the air volume contained within the fibres only partially take part in the acoustical absorption process. The fitted porosity according to Section 6.2.3 named the acoustically effective porosity are shown in Figure 6.5. The obtained acoustically effective porosity values were found to be lower than the measured porosity values, e.g. for 2 mm strand width the porosity is 15% lower at a density of 400 kg/m\(^3\). Moreover it was found that increasing the bulk density leads to a decrease of the open porosity, whereas the acoustically effective porosity increases when the bulk density increases. The latter can be caused by voids in the material that are being more efficiently used with regard to the sound absorption when they get smaller. The latter can be explained by the same principle as perforated panel absorbers, where the acoustic effective porosity is lower than the open pore fraction of the panels.
Based on the interpretation of the results, it was chosen to not use the measured porosity values, but to use the fitted acoustic effective porosity. This resulted in the regression lines presented in Figure 6.5. The RMSD-values of the found linear regression lines indicate the best possible fit having a maximum error of 2.67% as presented in Figure 6.5.

### 6.3.5 Flow resistivity

The results of the measured flow resistivity including the regression lines and the related RMSD-values are presented in Figure 6.6.

**Figure 6.6:** Exponential relation between the bulk density [kg/m$^3$] and the measured flow resistivity [Ns/m$^4$].
From Figure 6.6 it can be concluded that the strand width greatly influences the flow resistivity values. At the same density level, e.g. 400 kg/m³, the flow resistivity was lowest for the 1.0 mm strand width as a result of the higher binder amount present as indicated earlier. Consequently the flow resistivity was reduced due to the decrease of the wood wool strand volume. In case the wood-to-binder ratio of 1.0 mm would be the same as for the 1.5 and 2.0 mm strand width, it is expected that the curve would shift to the left from the 1.5 mm curve. The 1.5 mm strand width shows higher values than the 2.0 mm strand width because of the more refined pore structure due to the smaller strand width but higher amount of strands present. The 2.0 mm strand width WWCB was coarser and contained bigger openings between the strands since for the same wood volume, a lower amount of strands is present, which resulted in a lower flow resistivity.

6.4 Modelling results

6.4.1 Analysis of the inversely calculated input parameters for the JCA model

Tortuosity

Figure 6.7 presents the relation between the bulk density and the tortuosity, ratio between the path length a sound wave travels through the WWCB and the thickness of the WWCB (Cox and D’Antonio, 2009). In general, tortuosity mainly affects the position and height of the quarter-wavelength peaks (Wassilieff, 1996).

A higher WWCB density leads to a more complex path, resulting in a higher tortuosity, which is seen in Figure 6.7 for the three different strand widths. To make the WWCB acoustically thicker, a high value for the tortuosity is preferable. Therefore, it is important to notice the difference in slope of the regression lines for the three strands. This difference leads to a wider range in tortuosity values for the 1.5 and 2.0 mm strand.
compared to the 1.0 mm strand. Regarding the 1.0 mm strand width, tortuosity values were lower due to the used wood-to-binder ratio. When making use of the same density, the 1.5 mm WWCB was shown to show the highest tortuosity due to the increased amount of wood volume compared to the 1.0 mm strand width. In other words, regarding the tortuosity, an increased wood amount, up to a certain limit, is preferable compared to an increased binder amount. The presented RMSD-values for the 1.0, 1.5 and 2.0 mm width strands are 0.15, 0.13 and 0.16 respectively.

**Viscous characteristic length (Λ)**

The viscous characteristic length is the average radius in microns of the pores. It mainly describes the viscous effects at medium and high frequencies (Johnson et al., 1987). The values presented in Figure 6.8 show values within the 100-400 μm range and decreases with the increase of the density. These values are mainly representing the voids between the individual wood wool strands. As the amount of material increases, the characteristic length decreases.

![Figure 6.8: Relation between the density [kg/m$^3$] and the viscous characteristic length [μm] fitted by the JCA-model.](image)

**Thermal characteristic length (Λ’)**

The thermal characteristic length is the average radius in microns of the larger pores that are related to the thermal losses. Thermal characteristic length is two times the average pore volume to surface ratio of the pores (Leclaire, 2012). In Figure 6.9, the thermal characteristic length is presented for the 1.0, 1.5 and 2.0 mm and fluctuates between 200 and 300·10$^{-6}$ m in the density range of 275-550 kg/m$^3$. The RMSD-values for 1.0, 1.5 and 2.0 are 9.3, 19.7 and 12.9·10$^{-6}$ m, respectively.
6.4.2 Validation of the impedance model

In Figure 6.10, the relative prediction error is given for 30 different WWCB-samples extracted from three 25 mm thick boards with different strand widths (1.0, 1.5 and 2.0 mm) using the derived regression relations from Section 6.1. The implementation of the obtained relations in the JCA-model shows that the used impedance model was able to predict the normal incidence sound absorption of the three strand widths with the same order of accuracy as the errors from the all individual fitted results together of Figure 6.4.

Figure 6.10: Deviation of the predicted values by the JCA-model using the regression lines of Section 64.1 from the measured values (25 mm thick WWCB for (a) 1.0 mm; (b) 1.5 mm; (c) 2.0 mm strands.)
In Figure 6.11 the normal sound absorption curve for WWCB with a different thicknesses, 15 mm and 35 mm, are presented. The predicted values were based on the regressions relations discussed in Section 6.4.1. It can be observed that for all board types the error is less than 10% and that the 15 and 35 mm thicknesses are in good agreement with the measured results.

Figure 6.11: Predicted values by the JCA-model compared to the measured values for (a) d= 15 mm (1.5 mm strand width); (b) d= 35 mm (2.0 strand width).

6.5 Characterisation and optimization of the acoustical properties of WWCB

6.5.1 Influence of strand width
Table 6.2 illustrates the predicted sound absorption for WWCB with the same density and evaluate different strand widths (1.0, 1.5 and 2.0 mm). The input parameters required for the calculation are provided in Table 6.3 and are obtained from the regression lines on Section 6.4.1. It needs to be noted that the wood-to-binder ratios for the three strand widths are different, due to the different binder amount used per strand width. Therefore, the presented comparison only applies for the evaluated recipes. The SAA sound absorption of the 1.0 mm performs worse in comparison with the 1.5 and 2.0 mm because of the different microstructure caused by the different amount of wood and binder volume. The higher binder amount of the 1.0 mm samples results in a lower pore volume, tortuosity and flow resistivity. Moreover, the smaller strand width leads to a more refined pore structure and a higher acoustical effective porosity with lower thermal and viscous characteristic lengths. The 1.5 and 2.0 mm strand width WWCBs show comparable SAA sound absorption values of 0.36 and 0.35, respectively. A larger strand diameter leads to WWCB with larger openings and consequently a lower flow resistivity and tortuosity. Although the differences are relatively small, this results in a slightly lower sound absorption.
Table 6.2: Influence of three different strand widths for a board with a thickness of 25 mm and a density of 400 kg/m³ with their maximum sound absorption $\alpha_{n,max}$ and frequency $f_{an,max}$.

<table>
<thead>
<tr>
<th>Strand width [mm]</th>
<th>SAA-value [-]</th>
<th>$\alpha_{n,max}$ [-]</th>
<th>$f_{an,max}$ [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.31</td>
<td>0.93</td>
<td>2144</td>
</tr>
<tr>
<td>1.5</td>
<td>0.36</td>
<td>0.98</td>
<td>1521</td>
</tr>
<tr>
<td>2.0</td>
<td>0.35</td>
<td>0.96</td>
<td>1629</td>
</tr>
</tbody>
</table>

Table 6.3: WWCB parameters belonging to the normal incidence sound absorption values of Table 7.2.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>400</td>
<td>58</td>
<td>2795</td>
<td>1.99</td>
<td>191</td>
<td>204</td>
</tr>
<tr>
<td>1.5</td>
<td>400</td>
<td>65</td>
<td>4436</td>
<td>3.78</td>
<td>204</td>
<td>242</td>
</tr>
<tr>
<td>2.0</td>
<td>400</td>
<td>65</td>
<td>3400</td>
<td>3.38</td>
<td>216</td>
<td>242</td>
</tr>
</tbody>
</table>

6.5.2 Influence of the density

Table 6.4 presents the influence of the density on the modelled sound absorption of WWCB using three different strand widths. The presented density range was chosen based on the measured bulk density presented in Figure 6.2. Increasing the density (wood and binder amount) results in a higher flow resistivity, tortuosity and effective acoustical porosity, hence, a higher sound absorption. The increase in density leads to more efficient damping of the vibrations by viscous effects in the evaluated range. The results indicate that at least up to a density of 550 kg/m³ the sound absorption increases.

Table 6.4: Influence of the bulk density on the normal incidence sound absorption SAA values for 1.0, 1.5 and 2.0 mm strand widths with their maximum sound absorption $\alpha_{n,max}$ and frequency $f_{an,max}$.

<table>
<thead>
<tr>
<th>Density [kg/m³]</th>
<th>Strand width [mm]</th>
<th>SAA [-]</th>
<th>$\alpha_{n,max}$ [-]</th>
<th>$f_{an,max}$ [Hz]</th>
<th>SAA [-]</th>
<th>$\alpha_{n,max}$ [-]</th>
<th>$f_{an,max}$ [Hz]</th>
<th>SAA [-]</th>
<th>$\alpha_{n,max}$ [-]</th>
<th>$f_{an,max}$ [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>1.0 mm</td>
<td>0.27</td>
<td>0.91</td>
<td>2338</td>
<td>0.34</td>
<td>0.95</td>
<td>1672</td>
<td>0.32</td>
<td>0.92</td>
<td>1794</td>
</tr>
<tr>
<td>400</td>
<td>1.0 mm</td>
<td>0.31</td>
<td>0.93</td>
<td>2135</td>
<td>0.36</td>
<td>0.98</td>
<td>1522</td>
<td>0.35</td>
<td>0.96</td>
<td>1624</td>
</tr>
<tr>
<td>450</td>
<td>1.5 mm</td>
<td>0.34</td>
<td>0.96</td>
<td>1971</td>
<td>0.37</td>
<td>1.00</td>
<td>1400</td>
<td>0.37</td>
<td>0.99</td>
<td>1492</td>
</tr>
<tr>
<td>500</td>
<td>2.0 mm</td>
<td>0.36</td>
<td>0.97</td>
<td>1837</td>
<td>0.38</td>
<td>1.00</td>
<td>1308</td>
<td>0.39</td>
<td>1.00</td>
<td>1385</td>
</tr>
<tr>
<td>550</td>
<td>2.0 mm</td>
<td>0.39</td>
<td>0.99</td>
<td>1712</td>
<td>0.39</td>
<td>0.98</td>
<td>1237</td>
<td>0.40</td>
<td>1.00</td>
<td>1296</td>
</tr>
</tbody>
</table>

6.5.3 Optimization

Based on the results presented in the previous sections, an optimization study was performed. First of all it needs to be noted that the found relations between the bulk density and the input parameters of Section 7.4.1 for the JCA-model are determined within a specific range. These relations are extrapolated in this section, e.g. to analyse higher densities. Since such boards do not yet exist the results could not be validated. For the three different strand widths the following optimization studies were performed: (1) varying the board densities, (2) applying a density variation (multiple densities) and (3) implementation of air-cavities varying in thickness.
Board density

Figure 6.12 presents the extrapolated results of the three strand widths for a density range of 300-1000 kg/m$^3$. As expected from Section 6.5.2, increasing the density increases the sound absorption. However, when the density reaches a certain limit, the flow resistivity and tortuosity values become too high and viscous characteristic lengths becomes too low, resulting in a reduction of the overall sound absorbing properties. The moment of inclination differs per strand width, where 1.0 mm has its optimum sound absorption at about 800 kg/m$^3$, 1.5 and 2.0 are found to be 650 and 700 kg/m$^3$ respectively. It was found that increasing the density of a 25 mm WWCB will result in a maximum SAA-value of 64%, 40 and 27% for 1.0, 2.0 and 1.5, respectively. This densities can be created in practise when increasing the total binder and wood amount.

Figure 6.12: SAA-values for different densities for the three different strand widths (d=25 mm).

Density variations

Figure 6.13 presents the sound absorption of two 25 mm thick WWCBs with a density range of 200-1000 kg/m$^3$ attached to each other in which the dashed line represents a WWCB with a homogenous distribution of the thickness (same density per board). The results indicate a positive influence when the first layer contains a much lower density in comparison with the second layer. This means that construction has a stepwise increase of the impedance. For example, a 1.5 mm strand with a first layer of 300 kg/m$^3$ and a second layer of 800 kg/m$^3$ has a sound absorption of 0.6 while reversing the sample will lead to a sound absorption of 0.45, namely a reduction of 25%.
Figure 6.13: SAA-values presented in a contour plot for 2x 25 mm WWCB with varying densities for (a) 1.0 mm strand width; (b) 1.5 mm strand width; (c) 2.0 mm strand width.

Air cavity

Figure 6.14 presents the sound absorption of a 25 mm thick WWCB in the density range of 350-950 kg/m$^3$ with an air cavity of 25-200 mm. The contribution to the sound absorption using an air cavity was found to be especially positive in the low frequency range up to its maximum sound absorption level. For example, 1mm with a density of 800 kg/m$^3$ has without an air cavity (Figure 6.13) a SSA value of 0.5 while with an air cavity of 100 mm a value of 0.7 which is an improvement by 40%. Based on the results of Figure 6.14, in case of an unknown strand width, an overall air cavity is recommended to be 100 mm.

Figure 6.14: SAA-values presented in a contour plot for 25 mm WWCB with different densities and air cavities thicknesses using: (a) 1.0 mm strand width; (b) 1.5 mm strand width; (c) 2.0 mm strand width.
6.6 Conclusion

In this chapter which is based on the study of Botterman (2016) and Botterman et al. (2016), wood wool cement boards (WWCB) with varying strand widths, densities and thickness were acoustically characterized by means of an impedance tube and optimized using an impedance model applying different board densities, boards with a stepwise density. Furthermore, application of an air cavity was investigated. Based on the obtained results the following conclusions can be drawn:

- The Johnson-Champoux-Allard (JCA) model provides the best agreement with results obtained from the impedance tube and relations between the density of the WWCB samples and parameters of the JCA model have been successfully derived.
- Using the JCA model and obtained relations, the acoustic impedance of WWCB samples where obtained with low errors.
- The porosity can be better fitted from the measured values in the impedance tube than measured measuring it directly using a pycnometer since not all the voids in the wood wool and more importantly the voids between the wood wool strands are not effectively taking part in the sound absorption process.
- Increasing the density from 350 kg/m$^3$ to 550 kg/m$^3$ increases the sound absorption by 44, 14 and 25% for the 1.0, 1.5 and 2.0 mm strand width respectively. Above a density of 650, 700 and 800 kg/m$^3$ for 1.5 mm, 2.0 and 1.0 mm respectively, the sound absorption declines.
- Application of a multilayer WWCB with a stepwise density shows improved sound absorption in which the first layer should have a lower density compared to the second layer.
- When mounting a 25 mm WWCB on a rigidly backed air cavity, a width of 100 mm behind the board leads to the highest sound absorption for all investigated boards.
Chapter 7

Disposition after service life and treatment of biomass fly ashes


7.1 Introduction
In this chapter disposition of WWCB after its service life is considered following the waste hierarchy from re-use to disposal at landfill sites. Although in its current form the latter is rare, a more common end step is found to be energy recovery by incineration. Considering energy recovery, due to the large volume required for the incineration and the relative small waste volume of WWCB, the waste is often mixed with B-wood (Demolition wood, painted wood, chipboards, plywood) and organic products like dry paper sludge forming biomass. This combination leads to a new challenge namely: it generates contaminated fly ashes compared to the incineration of pure WWCB, forestry or agricultural waste. However, economically and environmentally it would be of interest to utilize the generated biomass fly ashes like the case of well-known pulverized coal combustion fly ash from the incineration of coal. However, the reuse of biomass fly ashes is restricted by their physical, chemical and environmental properties that depend on the type of raw material and incineration process parameters. In this study, four different biomass fly ash types produced by two different incineration plants were analysed and compared to Dutch and European standards on building materials. A combined treatment method was designed for lowering the leaching of contaminants and the effect of each treatment step was quantified. Finally, a pilot test was performed in order to scale up the treatment and make the biomass fly ashes suitable to be used in building materials.

7.2 Reuse, recycling and energy recovery
WWCB is a traditional building material applied for decades as an standalone board or as sandwich board. It can be found in many different applications ranging from indoor wall covering, acoustic ceilings, shuttering, sound barriers, sound baffles, reinforced roof boards, isolation of outside walls and wall elements. When the service lifetime of a construction comes to an end, the construction is destructed, creating demolition waste. Many elements of demolition waste can be recycled which is favourable following the waste hierarchy. The waste hierarchy sets an order of priority, staring with the preferred prevention, followed by re-use, recycling and energy recovery, with disposal (landfilling) as the last resort. Following the waste hierarchy is generally representing the most resource efficient and environmentally sound choice. In the WWCB industry, prevention
is already occurring during the production process, by selecting proper wood-logs, use of sharp knives and producing wood wool with sufficient thickness and moisture content that will not break as discussed in Chapter 2. Re-using or recycling increases in popularity but is not in all situations beneficial and strictly depends on the quality condition of the product and if the material has not been in contact with harmful substances during its use. The constitutes of WWCB i.e. the wood wool and binder are by them self-harmless. However, often the material is treated with paints or not applied as a standalone material, and can contain harmful substances leading to incineration for energy recovery.

### 7.2.1 Re-use

During recent years, WWCB are further developed following the transition from a building board to a design orientated board with different binders and strand thicknesses. Especially design boards applied in the indoor environment, keep their appearance for decades and after their lifetime it is easy to reuse by re-entering the market as a B-product. Moreover, recent trends direct towards cutting existing boards in different forms, sizes and colours to meet the demands of contemporary interior usage as presented in Figure 7.1.

![Figure 7.1: Examples of repurposed WWCB elements for interior usage (www.BAUX.com).](image)

### 7.2.2 Recycling

Reuse of the wood wool cement waste created during the production process of the WWCB or shredding the WWCB after its lifetime is very rare (van Elten, 2015). Reuse in the WWCB production can lead to production difficulties since the wood wool strands are often broken (making them too small) and the cement is already partially hydrated. However, for high density WWCB, boards that have sufficient thickness (> 50 mm) or in particle boards the mineralized wood wool strands can be potentially used as active filler when distributed equally over the board. Moreover, as described in Chapter 3 and Chapter 6, the addition of small particles can enhance the acoustical performance by refining the macro-pore area between the strands.

The current trends direct more into a cradle to cradle solution. Since 2016, a take-back scheme is offered to costumers by a WWCB producer named Troldtekt to turn in old WWCB products when purchasing new boards (www.troldtekt.com). For this, the user...
needs to assure that the Troldekt acoustic panels are not surface treated or in any other way contaminates during use. However, due to the long service lifetime (usually 50-70 years), it is currently not known if old boards are surface treated or absorbed contaminates from the surroundings during use. Therefore, most of these boards are classified as a demolition waste and end up in bio-energy power plants where biomass is incinerated. Moreover, the boards are suitable to be incinerated in cement kilns where the wood functions as fuel and the cement dehydrates and functions as new cement reducing the usage of raw materials.

7.2.3 Energy recovery

Especially the first generation of WWCB products are classified as building boards produced in the days when the manufacturing took place manually, meaning that the distribution in the moulds and lack of control means lead to production of quite poor quality boards. After its life time these boards are mainly incinerated due to their poor appearance and quality. When mechanical production became accepted, the number of different methods of application started to increase due to the higher quality of the boards and mass production that also led to processed wood wool cement boards as described in Chapter 1. Due to the increased quality, new combinations of wood wool cement boards were introduced like reinforced wood wool cement boards and sandwich boards consisting of a top layer of wood wool cement which is attached to insulation materials like mineral wool, PIR, EPS, XPS and Resol. Especially the reinforced wood wool cement boards became very popular being applied as roof layer on garages finished with bituminous roofing felt. The benefit was related to the lightweight construction and high thermal mass that reduced temperature of this type of buildings. However, reinforced WWCB are difficult to be recycled since the bitumen is solidly bonded. Therefore, the bituminous roof felt is milled off and the remaining composite is either used as soil conditioner but mostly incinerated.

Although recent developments and the awareness of recycling look very promising, a large portion of the WWCB products is simply incinerated and not even in a cement kiln where the binder can be dehydrated and reused and the wood can function as fuel. Being only a small portion of the yearly produced demolition waste, WWCB products are combined with other demolished waste products like B-wood, which includes painted, varnished and glued wood, or wood wool composite boards. Other compositions, such as paper sludge residue or organic municipal waste residues (food), are also used and together function as biomass fuel for incineration plants. The positive effect is that biomass can be used as a replacement of burning coal in power plants. These bio-power plants use the ‘waste’ or residue wood streams as fuel to produce heat, which is then consumed in steam turbines to generate electricity to be supplied to the electricity grid. From the incineration, fly ashes are generated which are collected and mainly disposed of at landfill sites. However, those responsible for the disposal of fly ash are regularly seeking potential ash utilization options because of high landfilling costs and the increasing banning of these on landfill sites (Keulen, 2015). Nowadays, pulverised coal fly ash is mainly applied in cement- and asphalt-based concrete mixtures due to its desirable physical and chemical properties. Since the fly ash is a fine material it is used as
filler in concrete mixtures. Also, due to its pozzolanic activity, it can be used as a binder to partly replace cement and therefore reduce the use of natural resources. In the Netherlands the majority of coal combustion fly ash is already applied in concrete (Vliegasunie, 2008).

However, the use of biomass as fuel in power plants leads to the production of fly ashes which are different from the ‘conventional’ coal combustion fly ash. These ashes created from burning biomass have different characteristics and properties in comparison to coal combustion fly ash. It has become important to find new ways for the reuse of biomass fly ashes, e.g. in concrete mixtures or as cement replacement in newly produced WWCB products. The fly ash obtained from the incineration of waste forest wood, agricultural waste and co-firing of biomass and other fuels has been investigated previously (Berra et al., 2015; Cheah and Ramli, 2011; Jaworek et al., 2013; Li et al., 2012; Lima et al., 2008; Pöykiö et al., 2009; Rajamma et al., 2015, 2009). However, the fly ash generated from the burning of contaminated wood has been studied less (Berra et al., 2015) and its reuse has not been started because of the following reasons:

1. biomass fly ash is a chemically and physically variable product, which makes its combination with cement more challenging. Its particle size distribution, loss on ignition, density, specific surface area, leaching, as well as pozzolanic/cementitious properties need to be tested to confirm its suitability;
2. biomass fly ash contains contaminants like lead, zinc and chromium and large amounts of chlorides from its raw materials and may have negative influences on the hydration of cement;
3. as replacement of cement, its slow pozzolanic activity influences the hydration process, consequently lowering the properties of concrete at early ages;
4. so far there is no certified treatment method to sufficiently remove the contaminants and increase the reactivity of contaminated fly ash, which could make its utilization more cost-efficient and sustainable.

The biomass fly ash created from burning biomass has different characteristics and properties in comparison to coal combustion fly ashes because of the different combustion input and therefore, additional research is needed to establish its applicability as building material. The first concern of such by-products is their environmental impact, and how it is evaluated based on the legislation (Landfill Ban Decree, 2012). In the case in which the fly ashes are considered hazardous or unfit for landfilling, a treatment must be envisaged before their disposal can take place. Furthermore, in order not to just lessen their environmental impact, but also to render such secondary materials useful, a number of other factors need to be taken into consideration like its physical and chemical properties.

Afterwards a number of utilization routes can be envisaged for these fly ashes, by comparison with the uses of coal combustion fly ash and other secondary building materials in WWCB and concrete mixes. A first of these routes is application as inert filler. A second application route is as secondary binder, in which case the chemical interactions between the biomass fly ashes and water and/or cement becomes of interest.
7.2.4 Environmental aspects and legislation

In the Netherlands, there are two legislative documents that regulate the use of waste materials – Landfill Ban Decree (Landfill Ban Decree, 2012) and the Soil Quality Decree (SQD) (2013). The Landfill Ban Decree classifies waste streams into inert, non-hazardous, hazardous and no landfill materials, according to their emission level. The Dutch Soil Quality Decree uses similar criteria to divide materials destined to be used in the built sector into non-shaped (granular), shaped (monolithic) and IBC building materials (which need to undergo insulation, management and control measures).

In order to evaluate the fly ash in terms of its environmental impact, a leaching test is performed. The leaching values for elements are determined by EN 12457 using a column percolation test. The emission values stated in the Landfill Ban Decree (2012) are defined by a relative amount of liquid to solid (L/S) of 10. However, this amount is hard to obtain for powder samples.

The fly ash can be seen as a waste or as building material; both products need to fulfill certain requirements. The Landfill Ban Decree (2012) contains requirements that classify waste streams into inert, non-hazardous and hazardous. If the sample does not fulfill these requirements, it cannot be used even for landfill before it undergoes a certain treatment.

If the fly ash is intended for application in building production it should also fulfill other requirements stated in the SQD (2013). According to the former, fly ash is a non-shaped building material because it is in powder form. When fly ash is applied into concrete blocks it will become a shaped building material. These concrete blocks will need to fulfill the requirements that are associated with shaped building materials.

The requirements of the SQD (2013) encompass maximum leaching values. The considered elements are those which are mainly available in building materials and can influence the soil quality.

The European standard EN 450 (2012) gives the criteria for the selection of fly ash; only fly ash with certain particle size (maximum 40% retention on the 45 μm sieve for class N and 12% for class S respectively) and chemical composition and loss on ignition values (under 5% for class A, between 2 and 7% for class B and between 4 and 9% for class C) can be used in concrete production. The ASTM C618 (2001) classifies fly ash based on the lime content. Two classifications of fly ash are produced, fly ash type C and type F, where the key difference between these classes is the amount of calcium, silica, alumina, and iron content in the ashes. Class C fly ash contains more than 20% lime, while it is less than 20% in type F fly ash, keeping in mind that the origin and properties of the combustion material are key factors that determine the parameters of the fly ash, and therefore its performance when added to the concrete mixture. Finally, the amount of fly ash determines the class of cement according to the EN 197-1 (2000) standard. Fly ash addition to concrete generally results in increased workability and, similar to ground granulated blast furnace slag, slow reactivity and increased strength over a long time. Also, the w/b ratio is reduced when fly ash is applied to the concrete mix. However, also in the case of coal combustion fly ash, the combustion method will highly influence the properties of the obtained ash (Chindaprasirt and Rattanasak, 2010).

Using fly ash to substitute cement in WWCB, concrete or using it as an filler can be beneficial for the environment, since landfilling is not required and less cement needs to
be produced. Moreover, the advantage of using fly ash in WWCB is its low density, leading to the implementation of more material that can cover the wood wool strands or produce a lower density product. In concrete mixtures it slows down the hydration process and so reduces the hydration heat accumulation, which benefits bulky constructions to reduce heat related cracking. However, the hydration of fly ash does take a longer time to start than Portland cement and therefore needs to be taken into account since it can reduce the early strength development.

The EN 450 (2012) gives criteria for coal combustion fly ash concerning properties like particle size distribution and chemical composition. It is stated that the pozzolanic activity of fly ash is determined by the content of SiO$_2$ and Al$_2$O$_3$, and that the reactive form of SiO$_2$ should be at least 25% (m/m). Additional requirements are:

1. Loss of ignition ≤ 5% (m/m);
2. Chloride content ≤ 0.10% (m/m) = 1000 (mg/kg);
3. Sulphate content ≤ 3.0% (m/m) = 30000 mg/kg;
4. Free calcium oxide ≤ 1.0% (m/m) = 10000 mg/kg.

Besides these, the maximum sieved residue on the 45 μm sieve is ≤ 40% (m/m).

### 7.3 Characteristics of the industrial by-product

#### 7.3.1 Materials

The biomass fly ashes used in this study were collected from the cyclone and electrostatic precipitators of two different power plants in the Netherlands. The reason for this approach is that fly ashes generated in power plants are inherently variable materials, because of several factors. Among these the type and mineralogical composition of the fuel, degree of pulverization, type of furnace and oxidation conditions including fuel ratio and the manner in which fly ash is collected, handled and stored before use are influential. Since no installations or plants have all of these factors in common, fly ash from various power plants are likely to be different. The following types of bio-power plant fly ash are examined (Table 7.1): boiler fly ash (BF1) and cyclone fly ash (BF2) from a plant in Hengelo (the Netherlands) and cyclone fly ash (BF3) and filter fly ash (BF4) from a plant in Alkmaar (the Netherlands). Using several types of fly ash, a more general approach of treatment and application can be sought.

Biomass fly ash can be classified by colour (Lima et al., 2008; Rajamma et al., 2009); this quality is important for aesthetic reasons but can also be used to distinguish particles that contain a large amount of iron oxide or unburnt coal. These particles are dark, blackish in colour and changes in their concentration can affect the overall colour of the fly ash. Figure 7.2 presents the four different biomass fly ashes investigated in this research. The BF1 and BF2 fly ashes are much darker than the BF3 and BF4 ones, which are attributed to carbon. The BF3 and BF4 fly ashes consist of agglomerated particles. The BF2 cyclone fly ash has a consistency more like fine powder (particle size under 0.125 mm) and the BF1 boiler fly ash – like a mix of fine powder and coal dust.
Because both incineration plants differ in incineration process the biomass ash can be distinguished by the colour classification, hence, the two incinerating processes are briefly discussed.

**Table 7.1:** Terminology of all fly ashes used in this study.

<table>
<thead>
<tr>
<th>Fly ash name</th>
<th>Fly ash type</th>
<th>Type of incineration bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF1</td>
<td>Boiler ash</td>
<td>Grill oven</td>
</tr>
<tr>
<td>BF2</td>
<td>Cyclone ash</td>
<td>Grill oven</td>
</tr>
<tr>
<td>BF3</td>
<td>Cyclone ash</td>
<td>Fluidized bed</td>
</tr>
<tr>
<td>BF4</td>
<td>Filter ash</td>
<td>Fluidized bed</td>
</tr>
<tr>
<td>R</td>
<td>Pulverised coal combustion fly ash</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 7.2:** Pictures of the four different fly ashes from both biomass power plants; (a) BF1; (b) BF2; (c) BF3; (d) BF4.

**The grill oven**

The grill oven in Hengelo consists of the following devices: moving tiles for the transport of waste materials; combustion zones; a water basin and an air suction system. The transport tiles can shift and tumble under an angle over each other. The waste undergoes various stages of the combustion process, like drying, degassing, and finally burning under temperatures around 850 °C. After a combustion time of around one hour, the solid combustion residues left on the grate (bottom ash) fall in a basin filled with water.

In general, a sufficiently high temperature (above 850 °C), the presence of oxygen (residual content of at least 6% in the flue gases), sufficient stand time (at least two seconds) and thorough mixing of the flue gases should provide a complete burning of the wood.

**The fluidized bed incinerator**

In this type of incinerator present in Alkmaar, the biomass is fed to the fluidized bed, which contains a large amount of sand (an inert, non-combustible material). A cyclone removes the solid and unburnt particles from the flue gases and carries it back to the bed.

There are two main types of fluidized beds. In the first one, the velocity is chosen so that the sand and the fuel just perform a bubbling motion. This can be called a stationary
fluidized bed or a bubbling fluidized bed (BFB). In the second type, the speed of the airflow is further increased creating flows that are carrying sand and fuel. Such an installation is called a circulating fluidized bed (CFB); this is the system used at the Alkmaar plant, which generated a part of the materials used in this study. Compared to a BFB, the CFB has the advantage that by the greater turbulence the heat transfer will be higher, which means a lower flue stream resulting in a highly efficient system. The disadvantages of the CFB are the higher use of electric power due to the need for an increased airflow and the higher dust concentration in the flue gas. Most of the dust, however, is simply separated from the flue gas in the cyclone. Unburnt particles from the flue gases are going back to the combustion chamber. That process is controlled by the cyclone. After this, there is another cyclone that captures red-hot ash particles and ash particles greater than 10 μm. The fly ash that is removed by the cyclone is stored in closed fly ash silos.

In general, fly ashes in the grill oven are collected in the following way: coarser particles in the boiler, finer particles in the electrostatic filter and in the cloth filter. In the fluidized bed incinerator, fly ash is collected as follows: coarser particles in the cyclone and finer particles in the electrostatic filter.

7.3.2 Leaching

The leaching values of the different fly ashes from the bio-power plant compared to the classifying values for L/S = 10 according to the Soil Quality Regulation (2013) are presented in Table 7.2. It can be seen that all the employed biomass fly ashes qualify as hazardous (BF1, BF2 and BF3) or no-landfill (BF4). The values in italics represent the “non-hazardous” category, the ones in bold belong to the “hazardous” class and the underlined ones to the “no landfill” one.

The chloride, chromium, lead and sulphate contents are above the limit, which means that the fly ashes cannot go to landfill before having a pre-treatment to remove unwanted elements. The cleaning process can be a chemical treatment, immobilization using binders or washing techniques, of which the latter is used in this study. In case it is impossible to fulfil all the non-shaped building material requirements it can be used in a shaped building material; part of the elements will then be immobilized and therefore not account for hazardous substances anymore (van Eijk, 2001).

7.3.3 Particle size distribution

Fineness is one of the primary physical characteristics of fly ash that relates to its pozzolanic activity (Joshi, 1970). When examining fly ash for its particle size distribution (PSD) the EN 450 sets the limit of 40% for the maximum amount of fly ash retained on the 45 μm mesh sieve on wet sieving, as a quality control measure. The fly ashes BF1 and BF2 examined with the Mastersizer are sieved to a maximum particle size of 250 μm. However, from the results presented in Table 7.3, about 10% of the particles still have a larger size. This is due to the fact that some particles are needle-shaped, so when falling vertically they will slip through the sieve mesh openings. For using fly ash as filler, fly ash should contain fine spherical particles instead of the fused forms. So far BF4 fulfils this requirement and the requirements of EN 450 for maximum retained fly ash on the 45 μm sieve.
Table 7.2: Classification of inert, non-hazardous, hazardous and no-landfill elements in the fly ashes (L/S = 10, column test EN 12457) according to the Landfill Ban Decree (2012) in mg contaminant/kg dry matter. Values for the analyzed biomass fly ashes are presented, obtained in 2010 for BF1 and BF2 and in 2011 for BF3 and BF4, together with the range in parentheses, when available. The values in italics represent the “non-hazardous” category, the ones in bold belong to the “hazardous” class and the underlined ones to the “no landfill” one.

<table>
<thead>
<tr>
<th></th>
<th>Inert (mg/kg)</th>
<th>Non-hazardous (mg/kg)</th>
<th>Hazardous (mg/kg)</th>
<th>No Landfill (mg/kg)</th>
<th>BF1 (mg/kg)</th>
<th>BF2 (mg/kg)</th>
<th>BF3 (mg/kg)</th>
<th>BF4 (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>&lt;0.06</td>
<td>0.06-0.7</td>
<td>0.7-5</td>
<td>&gt;5</td>
<td>&lt;0.3 (0.3-0.6)</td>
<td>&lt;0.3 (0.3-0.6*)</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>As</td>
<td>&lt;0.5</td>
<td>0.5-2</td>
<td>2-25</td>
<td>&gt;25</td>
<td>&lt;0.6 (0.48*0.6)</td>
<td>&lt;0.6 (0.5*0.6)</td>
<td>&lt;0.6</td>
<td>&lt;0.6</td>
</tr>
<tr>
<td>Ba</td>
<td>&lt;20</td>
<td>20-100</td>
<td>100-300</td>
<td>&gt;300</td>
<td>&lt;3 (1.1*3.1)</td>
<td>&lt;3 (2.1<em>9.1</em>)</td>
<td>5.68</td>
<td>20.9</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt;0.04</td>
<td>0.04-1</td>
<td>1-5</td>
<td>&gt;5</td>
<td>&lt;0.3 (0.02*0.3)</td>
<td>&lt;0.3 (0.02*0.3)</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;800</td>
<td>800-1500</td>
<td>15000-25000</td>
<td>&gt;25000</td>
<td>2400 (1647<em>5764</em>)</td>
<td>8300 (7200<em>34314</em>)</td>
<td>21000</td>
<td>8000</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;0.5</td>
<td>0.5-10</td>
<td>10-70</td>
<td>&gt;70</td>
<td>13.9 (0.8*13.9)</td>
<td>15.4 (0.23<em>23.3</em>)</td>
<td>&lt;3</td>
<td>&lt;3</td>
</tr>
<tr>
<td>F</td>
<td>&lt;10</td>
<td>10-150</td>
<td>150-500</td>
<td>&gt;500</td>
<td>&lt;50 (4.5*50)</td>
<td>&lt;50 (16.9*50)</td>
<td>&lt;50</td>
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<td>Cu</td>
<td>&lt;2</td>
<td>2-50</td>
<td>50-100</td>
<td>&gt;100</td>
<td>&lt;1.5 (0.2*1.5)</td>
<td>&lt;1.5 (0.22*1.5)</td>
<td>&lt;1.5</td>
<td>&lt;1.5</td>
</tr>
<tr>
<td>Hg</td>
<td>&lt;0.01</td>
<td>0.01-0.2</td>
<td>0.2-2</td>
<td>&gt;2</td>
<td>&lt;0.07 (0.003*0.07)</td>
<td>&lt;0.07 (0.003*0.07)</td>
<td>&lt;0.07</td>
<td>&lt;0.07</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;0.5</td>
<td>0.5-10</td>
<td>10-50</td>
<td>&gt;50</td>
<td>28.8 (2.8-28.8)</td>
<td>528 (30.37*)</td>
<td>50</td>
<td>315</td>
</tr>
<tr>
<td>Mo</td>
<td>&lt;0.5</td>
<td>0.5-10</td>
<td>10-30</td>
<td>&gt;30</td>
<td>&lt;3 (2.2<em>3.7</em>)</td>
<td>&lt;3 (2.4<em>4.2</em>)</td>
<td>&lt;3</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;0.4</td>
<td>0.4-10</td>
<td>10-40</td>
<td>&gt;40</td>
<td>&lt;3 (0.23*3)</td>
<td>&lt;3 (0.23*3)</td>
<td>&lt;3</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;0.1</td>
<td>0.1-0.5</td>
<td>0.5-7</td>
<td>&gt;7</td>
<td>&lt;0.07 (0.15*0.22)</td>
<td>&lt;0.15 (0.15<em>2.2</em>)</td>
<td>0.161</td>
<td>0.358</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>&lt;1000</td>
<td>1000-2000</td>
<td>20000-50000</td>
<td>&gt;50000</td>
<td>19000 (17940*20000)</td>
<td>14950*15000</td>
<td>35881*</td>
<td>20000</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;4</td>
<td>4-50</td>
<td>50-200</td>
<td>&gt;200</td>
<td>10.9 (3.9-19.5)</td>
<td>32.5 (11.4*36.1)</td>
<td>11</td>
<td>14.5</td>
</tr>
</tbody>
</table>

*Value recalculated from a different L/S ratio.

Table 7.3: PSD characteristics of all four bio fly ashes and the reference powder coal fly ash, before and after treatment (notations from Table 7.7).

<table>
<thead>
<tr>
<th></th>
<th>BF1</th>
<th>BF2</th>
<th>BF3</th>
<th>BF4</th>
<th>R</th>
<th>BF1-T1</th>
<th>BF1-T2</th>
<th>BF2-T</th>
<th>BF3-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_min (µm)</td>
<td>1.7</td>
<td>2.2</td>
<td>0.7</td>
<td>0.7</td>
<td>0.6</td>
<td>0.8</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>d₁₀ (µm)</td>
<td>18</td>
<td>8.7</td>
<td>10</td>
<td>3.8</td>
<td>5.0</td>
<td>5.0</td>
<td>4.0</td>
<td>4.0</td>
<td>7.0</td>
</tr>
<tr>
<td>d₃₀ (µm)</td>
<td>110</td>
<td>110</td>
<td>38</td>
<td>13</td>
<td>25</td>
<td>31</td>
<td>31</td>
<td>34</td>
<td>34</td>
</tr>
<tr>
<td>d₅₀ (µm)</td>
<td>138</td>
<td>130</td>
<td>47</td>
<td>19</td>
<td>30</td>
<td>40</td>
<td>40</td>
<td>42</td>
<td>46</td>
</tr>
<tr>
<td>d₇₀ (µm)</td>
<td>202</td>
<td>187</td>
<td>75</td>
<td>40</td>
<td>106</td>
<td>63</td>
<td>63</td>
<td>68</td>
<td>80</td>
</tr>
<tr>
<td>d₁₀₀ (µm)</td>
<td>255</td>
<td>235</td>
<td>110</td>
<td>69</td>
<td>120</td>
<td>82</td>
<td>83</td>
<td>90</td>
<td>113</td>
</tr>
<tr>
<td>D_max (µm)</td>
<td>479</td>
<td>417</td>
<td>631</td>
<td>209</td>
<td>832</td>
<td>158</td>
<td>158</td>
<td>182</td>
<td>275</td>
</tr>
</tbody>
</table>

7.3.4 X-Ray Fluorescence spectroscopy

Table 7.4 lists the mass percentages of the most important oxides present in the analysed samples of the biomass fly ashes, while Table 7.5 presents the maximum and minimum values of the concentrations of the main contaminants for the four different biomass power plant fly ashes, also obtained by XRF. These main contaminants were chosen based on leaching tests, as described above. The samples for the concentration measurements are collected twice per year at the corresponding power plant. It can be seen that for each plant the concentration of the components varies. This is due to the different fuel types, the combustion process and the collecting point of each plant, as indicated before. The content of all elements is reported in milligrams of element per kilogram of dry sample (mg/kg ds).
### Table 7.4: Oxide composition of the four fly ash types obtained by XRF, compared to that of coal combustion fly ash; LOI determined under oxidizing atmosphere is also included.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>BF1 (% mass)</th>
<th>BF2 (% mass)</th>
<th>BF3 (% mass)</th>
<th>BF4 (% mass)</th>
<th>R (% mass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>33.2</td>
<td>28.5</td>
<td>30.9</td>
<td>49.7</td>
<td>4.7</td>
</tr>
<tr>
<td>SiO₂</td>
<td>22.2</td>
<td>33.3</td>
<td>19.1</td>
<td>6.6</td>
<td>52.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.7</td>
<td>4.8</td>
<td>7.1</td>
<td>2.7</td>
<td>21.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.7</td>
<td>5.7</td>
<td>4.4</td>
<td>2.7</td>
<td>9.7</td>
</tr>
<tr>
<td>SO₃</td>
<td>7.7</td>
<td>6.5</td>
<td>10.5</td>
<td>11.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Cl</td>
<td>0.82</td>
<td>1.18</td>
<td>4.24</td>
<td>8.02</td>
<td>0.00</td>
</tr>
<tr>
<td>Remaining oxides</td>
<td>23.0</td>
<td>16.3</td>
<td>19.1</td>
<td>13.0</td>
<td>7.9</td>
</tr>
<tr>
<td>LOI (oxidizing atmosphere)</td>
<td>2.7</td>
<td>3.7</td>
<td>4.7</td>
<td>5.7</td>
<td>1.7</td>
</tr>
</tbody>
</table>

### Table 7.5: Contaminants concentration ranges of the four bio fly ashes obtained by XRF.

<table>
<thead>
<tr>
<th>Element</th>
<th>BF1 (mg/kg ds)</th>
<th>BF2 (mg/kg ds)</th>
<th>BF3 (mg/kg ds)</th>
<th>BF4 (mg/kg ds)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony (Sb)</td>
<td>28-49</td>
<td>65-300</td>
<td>67</td>
<td>110</td>
</tr>
<tr>
<td>Bromide (Br⁻)</td>
<td>15-59</td>
<td>15-150</td>
<td>130</td>
<td>420</td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>990-5600</td>
<td>5300-27000</td>
<td>23000</td>
<td>83000</td>
</tr>
<tr>
<td>Fluoride (F⁻)</td>
<td>2-6.8</td>
<td>6.9-100</td>
<td>5</td>
<td>2.1</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>210-380</td>
<td>210-620</td>
<td>830</td>
<td>890</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>4.6-5.8</td>
<td>7.1-13</td>
<td>8.8</td>
<td>11</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>&lt;4</td>
<td>4-9.4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Sulphate (SO₄²⁻)</td>
<td>9800-15000</td>
<td>11000-16000</td>
<td>7200</td>
<td>6100</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>23-27</td>
<td>39-45</td>
<td>39</td>
<td>30</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>1100-3300</td>
<td>2700-10000</td>
<td>4600</td>
<td>3000</td>
</tr>
</tbody>
</table>

#### 7.3.5 X-Ray Diffraction

XRD provides information about the mineral composition of the fly ashes (Figure 7.3). The reference coal combustion fly ash is mainly constituted of quartz (SiO₂), hematite (Fe₂O₃) and mullite (2Al₂O₃•SiO₂). Quartz is also the main constituent of all the four investigated fly ashes, followed by Ca-containing compounds (CaSO₄, CaCO₃, CaO or Ca(OH)₂) and TiO₂ in various crystalline phases. These results are in line with the findings of (Cheah and Ramli, 2011; Elinwa and Ejeh, 2004; Elinwa and Mahmood, 2002; Campbell, 1990; Etiégni and Campbell, 1991). Chlorides were hard to detect by XRD, being in too low quantity to be clearly visible (phases under 10% by mass are expected to be hard to identify). Still, the BF4 fly ash diffractograms permitted the identification of halite (NaCl) due to its high Cl quantity shown by XRF. The largest fraction of BF1 (particles larger than 500 μm) were also expected to contain a high amount of chlorides and indeed, NaCl could also be observed by XRD as present in its mineralogical composition.
Disposition after service life and treatment of biomass fly ashes

Figure 7.3: (a) X-Ray diffractograms of the R (reference) and BF1, BF1>500μm and BF2 bio fly ashes; (b) X-Ray diffractograms of the R (reference), BF3 and BF4 bio fly ashes.

CaSO$_4$ (▲); 2Al$_2$O$_3$•SiO$_2$ (○); TiO$_2$ (●); SiO$_2$ (■); Ca(OH)$_2$ (△); CaCO$_3$ (◆); Fe$_2$O$_3$ (□); NaCl (◇); CaO (★); K-containing phase of the type K$_2$Pb$_2$(CrO$_4$)$_3$ or K$_2$Ca$_2$(SO$_4$)$_3$ (x).

### 7.3.6 Treatment steps

The treatment steps defined in this research depend on the biomass fly ash and moreover the compounds which it contains. In general the following treatment methodology is used: Firstly, carbon particles are removed, because of the negative effect on the chloride removal. Secondly, the fly ash is washed to reduce the soluble chlorides and aluminium content and in the end grinding can be performed to decrease the PSD and possibly increase the reactivity of the biomass fly ashes. A schematic overview of the treatment steps is provided in Figure 7.4.
Figure 7.4: Treatment methodology.
**Sieving**

This treatment is needed for biomass fly ashes with a high content of carbon. Using a sieve of 500 μm, coarse carbon particles will be removed. In this way the LOI will be reduced, as well as the chloride content of the fly ash as illustrated in Figure 7.5. It is found that BF1 boiler fly ash consists of 13.1% coarse carbon particles (above 500 μm, a discarded fraction) and the carbon particles also remain in the lower sieve diameters as illustrated in Figure 7.5. However, the BF2 cyclone fly ash has only 0.7% coarse carbon particles larger than 500 μm and the carbon particles are almost entirely filtered out using the 125 μm sieve diameter. The remaining fly ash <125 μm constitutes 41.5% of the total amount of fly ash, which means that it is much more suitable as an active filler or as cement replacement than the BF1, based on its finer particles that are reacting faster and have less/non carbon content. All four BFA samples have LOIs between 2.7 and 5.7% (Table 7.4), which are lower than other types of forestry ashes (Girón et al., 2013, 2012).

![Figure 7.5: Sieved ash from 500 to <125 μm for (a) BF1; (b) BF2.](image)

**Thermal treatment and air-filtering**

This treatment is needed for biomass fly ashes with a high content of fine carbon particles (< 40 μm). These fly ashes can be recognized by their black appearance, even after sieving (treatment 1). For this treatment, two options (2a and 2b) are available: treatment 2a is a thermal treatment (Kuboňová et al., 2013; Lindberg et al., 2015) and treatment 2b is a separation by electrostatic filters (both for industrial use). However, in the laboratory the thermal treatment is performed by using an oven and electrostatic filters are replaced by a shaking device with air suction. These measures should provide similar end results as the above described industrial processes. The choice of which method to use depends on whether there are mineral phases present that can change when a thermal treatment is used.

If there is a potential of a phase change, treatment 2a is not an option and treatment 2b can be applied. Treatment 2b uses a shaking mechanism with air exhaust. By shaking, the light coal particles are lifted and removed using the air exhaust. When well calibrated, the removal of fine light particles that are not coal should be limited.
Washing optimization

In order to investigate the quantity of chloride which is removed from solid boiler fly ash BF1 by distilled water, the chloride content of BF1 is determined by the following method: Two grams solid material (biomass fly ash), together with 37 ml of demineralised water and 3 ml of nitric acid is combined in a bottle. The mix is then stirred using a magnetic stirrer on a heating plate of 45 °C for 15 min. Afterwards, the solution is filtered and flushed with demineralised water until a volume of filtrate of 100 ml is obtained. From this, 2-10 ml, depending on the chloride content, can be measured using Metrohm 785 DMP Titrino with a 0.01 M solution of silver nitrate.

This is done for two pairs of measurements, a plain BF1 without any changes and a ground BF1. Furthermore, a sample has been sieved on a 500 μm and then the two subsequent fractions ground.

The plain BF1 samples were found to contain less chlorides than the ground samples (2882±455 and 3714±58 mg Cl/kg BF1 respectively), probably because not all chloride ions from the former were dissolved (some chloride ions contained in larger coal particles were not dissolved in water, which also explains the larger standard deviation for the samples which were not ground). The sample retained on the 500 μm sieve represents 13% by mass of the BF1 sample before sieving and was found to have the greatest chloride content (18236 mg Cl/kg BF1 above 500 μm). The counterpart samples under 500 μm were measured to contain 3282 mg Cl/kg BF1 under 500 μm; it is believed that these two samples together give a good representation, giving a total chloride content of 5225 mg/kg BF1 which will be used further on as a base value. Moreover, this value is close to the results from the XRF analysis (5600 mg/kg BF1). These results show that coal particles have a large influence on the chloride content of fly ash.

The same procedure was followed for the BF2 sample, analysing both plain and ground samples. It is shown that the differences between the two samples were much lower (4061±197 mg/kg BF2 for the plain samples and 4130±35 mg/kg BF2 for the ground ones). This is probably due to smaller content of carbon particles (just 0.7% by mass over 500 μm) and the initial chloride content will be from now on considered to be 4131 mg Cl/kg BF2 fly ash.

Samples BF3 and BF4 are much finer (Table 7.3) and also have no apparent unburnt carbon content (Figure 7.2), so their chloride content was also more stable and did not require grinding the samples in order to achieve the maximum chloride measurement. The initial chloride contents for these samples that will be used from now on are 19526 mg/kg BF3 and 86103 mg/kg BF4.

In order to optimize the washing process, different treatment parameters and their influence on the BF1 fly ash properties are investigated. In this case the fly ash is shaken for one hour with different water of different temperatures (20 and 60 °C), two different shaking speeds (120 and 240 rpm) and two different liquid to solid ratios (L/S = 2, L/S = 4 (Colangelo et al., 2012)). The remaining chlorides are measured by taking three ml of the leachate and measuring the chloride content by titration. The results are given in
Table 7.6 and they present an improvement by increasing the shaking speed compared to the original, especially for an L/S ratio of two.

**Table 7.6:** Removed chlorides from boiler fly ash BF1 with different parameters (percentage removed is calculated from the original 5226 mg/kg).

<table>
<thead>
<tr>
<th></th>
<th>20 °C, 120 rpm (mg/kg)</th>
<th>20 °C, 240 rpm (mg/kg)</th>
<th>60 °C, 120 rpm (mg/kg)</th>
<th>60 °C, 240 rpm (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Cl removed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L/S = 2</td>
<td>37.4</td>
<td>49.3</td>
<td>40.0</td>
<td>54.9</td>
</tr>
<tr>
<td>% Cl removed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L/S = 4</td>
<td>39.1</td>
<td>44.4</td>
<td>44.4</td>
<td>51.7</td>
</tr>
</tbody>
</table>

**Separation/Grinding**

This last treatment method is used to reduce the size of the particles using a ball mill (only for laboratory use), at the same time increasing the reactivity of the particles.

### 7.4 Treatment results of biomass fly ash and a pilot washing test

#### 7.4.1 Leaching results

**BF1 boiler fly ash**

To ensure that the maximum chloride content will not exceed 1000 mg/kg (according to EN 450) as mentioned in Section 7.3.2, the following treatment steps are carried out:

1. The biomass fly ash is sieved on a 500 μm sieve to remove large coal particles (S);
2. The biomass fly ash is:
   a. air filtered to remove fine coal particles (AF);
   b. thermally treated at 750 °C to incinerate fine coal particles (H).
3. The biomass fly ash is then washed using the water treatment (W).

The results are illustrated in Figure 7.6a. Through the first step, the available chloride content is already reduced by 45%. This is due to absorbed chloride and chlorine in the carbon structure. Washing this fly ash will result in a total decrease of 51%. This is 6% lower than the case without washing, from which it can be concluded that washing has rather limited effect as long as fine carbon particles are still present. The soluble chlorides are probably attached to the surface of the carbon particles and thus prevented to dissolve in water. Removing the fine carbon particles using Treatment 2a or 2b results in a reduction of 75% and 70%, respectively, compared to the original fly ash; washing these fly ashes results in a total chloride reduction of 93% and 82% respectively. This indicates that removing the coal particles increases the removal of chlorides.
Figure 7.6: Chloride ions in (a) BF1 boiler fly ash before and after different treatment steps (notations from Table 7.7); (b) the BF2 cyclone fly ash before and after different treatment steps.

Figure 7.7: Chloride ions in the (a) BF3 cyclone fly ash; (b) BF4 filter fly ash before and after treatment.
**BF2 cyclone fly ash**

Since this fly ash only has large carbon particles the following steps are performed:
1. The biomass fly ash is sieved on a 500 μm sieve, to remove large coal particles;
2. The biomass fly ash is washed using the water treatment.

The results are illustrated in Figure 7.7b.

The chlorides in BF2 ash are very soluble and after just the washing treatment the fly ash almost fulfils the maximum limit of 1000 mg/kg. When sieved on a 500 μm sieve, the chloride content is reduced by 12%. After sieving on a 500 μm sieve and water treatment only 9% of the chloride content remains, compared to 29% when washed without sieving. This means that by removing carbon the efficiency of the treatment increased significantly and as a result the chloride content fulfils the stated requirements.

**BF3 cyclone fly ash**

This fly ash has no carbon content issues and therefore the water treatment could immediately be applied to fulfil the chloride requirements (Figure 7.8a). However, because of the observed reaction of metallic aluminium, the washing treatment was prolonged for 72 h, using an L/S = 4. After washing the chloride content is reduced by 96% and fulfils the stated requirements.

**BF4 filter fly ash**

This fly ash does not contain carbon particles (like BF3) and therefore can immediately be water-treated. It also contains metallic aluminium, but because the water treatment was not successful further research has not been performed. As it can be seen from Figure 7.8b, the chloride content of this fly ash is 86 times more than allowed. After treatment this amount is reduced by 80% but still it is too high to be used as cement replacement in concrete structures.

**Final treated samples**

After investigating the chloride content decrease of all the treatment options on all four bio fly-ashes, the final treatment method for each of these was selected. In the case of BF1, two treatment routes were chosen, both through air-filtering and heating; therefore, two treated samples will be investigated further, and termed BF1-T1 and BF1-T2. The BF2 and BF3 fly ashes each undergo only one treatment route and therefore the final treated samples will from here onwards be termed BF2-T and BF3-T. The BF4 sample will not be investigated further, as explained earlier.

Table 7.7 summarizes the treatment steps undergone by the BF1, BF2 and BF3 samples before being considered useable as non-shaped materials in concrete. Incompletely-treated samples (the ones that underwent only part of the treatment steps) will still be referred to using the abbreviation for the used treatments, as also mentioned in Table 7.7. For instance, a BF1 sample which has only been sieved will be termed BF1-S, while a BF1 sample which underwent sieving (S), heating (H) and washing (W), but not grinding (G), will be termed BF1-S/H/W.
Table 7.7: Treatment steps undergone by the BF1, BF2 and BF3 samples before being used as cement replacement.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>BF1-T1</th>
<th>BF1-T2</th>
<th>BF2-T</th>
<th>BF3-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sieving &lt; 500 μm (S)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
</tr>
<tr>
<td>Air-filtering (AF)</td>
<td>X</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heating (H)</td>
<td>-</td>
<td>X</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Washing (W)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Grinding (G)</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>-</td>
</tr>
</tbody>
</table>

7.4.2 Composition and fineness

In Figure 7.8a the effect of both thermal treatment (BF1-S/H) and air filtering (BF1-S/AF) on the PSD of the fly ashes are illustrated, together with the original PSD of the BF1 boiler fly ash which was sieved to under 500 μm, BF1-S. Also ground BF1 (BF1-S/AF/G and BF1-S/H/G) which fulfil the EN 450 are presented and will be used for strength development in the following sections. It can be seen that the thermal and the air filtering treatment yield almost the same PSD. Both PSDs are shifted to the right, indicating coarser particles due to the removal of the fine coal particles. Looking at the ground fly ash, 65% is smaller than 45 μm, fulfilling the stated requirements concerning fineness.

The effect of the water treatment on the PSD of this fly ash is illustrated in Figure 7.8b. To obtain these results, the fly ash is first heated and ground (BF1-S/H/G) and afterwards is water treated for comparison (BF1-T2). The effect of the water treatment is negligible and only the soluble materials that are removed provide a small change in the PSD.

Figure 7.8: PSDs (a,b) BF1 before and after different treatment steps.
Both BF2 and BF3 are water treated and ground. The results are presented in Figure 7.9. Also these two biomass fly ashes are fulfilling the stated requirements after successfully being water treated and ground. The data described in Table 7.3 indicates that even after grinding of the biomass fly ashes, the reference fly ash still has a smaller PSD and a larger SSA. However, there is a large improvement after treatment (all $d_{10}$, $d_{50}$ and $d_{90}$ decrease when compared to the original values).

Table 7.8 presents the oxide composition of the final treated samples, together with the LOI values. The reduction in Cl content is very clear, the final values detectable by XRF being extremely low in comparison to the ones presented in Table 7.4. The LOI of all samples is also reduced, as expected. Except for BF2-T, all other final treated biomass fly ashes do not comply with the requirement of $\text{LOI} < 5\%$ (Section 7.2.3). This is due to the formation of $\text{Ca(OH)}_2$ during washing, which is then decomposed at around $450 \, ^\circ\text{C}$. However, this criterion was used in this study solely for comparison purposes, and the formed portlandite is not expected to be detrimental in the case of using these treated biomass fly ashes as concrete ingredients.

**Table 7.8.** Oxide composition of the final treated fly ash types obtained by XRF.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>BF1-T1</th>
<th>BF1-T2</th>
<th>BF2-T</th>
<th>BF3-T</th>
<th>BF4-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>29.1</td>
<td>28.2</td>
<td>27.1</td>
<td>31.0</td>
<td>48.9</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>28.5</td>
<td>29.3</td>
<td>33.3</td>
<td>18.9</td>
<td>8.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>4.2</td>
<td>4.6</td>
<td>4.7</td>
<td>5.8</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>6.5</td>
<td>5.6</td>
<td>6.2</td>
<td>6.0</td>
<td>2.9</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>6.7</td>
<td>6.2</td>
<td>4.7</td>
<td>11.7</td>
<td>12.4</td>
</tr>
<tr>
<td>Cl</td>
<td>0.05</td>
<td>0.14</td>
<td>0.04</td>
<td>0.04</td>
<td>0.97</td>
</tr>
<tr>
<td>Remaining oxides</td>
<td>18.2</td>
<td>18.2</td>
<td>15.3</td>
<td>16.9</td>
<td>12.7</td>
</tr>
<tr>
<td>LOI (oxidizing atmosphere)</td>
<td>6.7</td>
<td>7.7</td>
<td>8.7</td>
<td>9.7</td>
<td>10.7</td>
</tr>
</tbody>
</table>

X-ray diffraction on BF4 was used to identify the chloride phases which can be removed through the washing process. For this purpose, the BF4 diffractograms of the original fly ash and the washed one (BF4-W) were subtracted, in order to highlight only certain changes. The BF4 sample was chosen for containing the largest amounts of chlorides.
both before and after washing (Figure 7.10), therefore increasing the chance of observing
the changes on a diffractogram more clearly.
BF4 contains phases like anhydrite (CaSO₄), portlandite (Ca(OH)₂), quartz (SiO₂),
chlorides (CaCl₂ and NaCl) and calcite (CaCO₃), which were detailed in Section 7.3.5.
After the water treatment the structure is similar and there is a visible increase in the
height of the peaks of Ca(OH)₂ and a decrease of the height of the peaks of all the four
investigated chlorides (NaCl, KCl, CaCl₂ and MgCl₂).

![Figure 7.10: XRD pattern of original BF-4 and water treated BF4-W highlighting just the chloride peaks: MgCl₂ (■), KCl (▲), NaCl (◆) and CaCl₂ (●).]

### 7.4.3 Final leaching estimation of the treated bio fly ashes

The treated samples, BF1-T1, BF1-T2, BF2-T and BF3-T were tested for the leaching of
contaminants to fulfil the stated requirements, before attempting their use as cement
replacement in WWCB and concrete. However, because the standard leaching test (Soil
Quality Regulation, 2013) is time-consuming, an accelerated test was performed. The
four treated samples were washed for 24 h with water, with an L/S ratio of 10 and a
shaking speed of 240 rpm. The leachate was then analysed and the results are presented
in Table 7.9.

The results of this leaching test are expected to be much higher than the usual column
leaching test, due to the shaking of the samples for 24 h at high rotational speed.
Therefore, the values are not directly comparable to the ones presented in Table 7.2.
However, these values will be compared with the non-shaped building materials
requirements according to the Soil Quality Regulation (2013), trusting that these values
will be lower than the column test ones.

It can be observed from Table 7.9 that only the antimony, chromium and sulphate levels
are still over the legal limit (values in bold). In all cases, the leached chlorides are well
under the legal limit. In the case of both antimony and chromium, the leaching values
were under or very close to the legal limits even before the treatment steps (see Table
7.2), so it is assumed that this will continue to be the case with the final treated samples.
The very much decreased chloride leaching levels achieved using the above-described
method prove promising that all the rest of the maximum contaminant leaching values will also be met.

Table 7.9: Results of the 24 h leaching test on the final treated bio fly ashes and non-shaped building material requirements compared with the fly ash values (L/S = 10) according to the Soil Quality Decree (2013).

<table>
<thead>
<tr>
<th>Element/Ion</th>
<th>Non-shaped building materials (mg/kg)</th>
<th>BF1-T1 (mg/kg)</th>
<th>BF1-T2 (mg/kg)</th>
<th>BF2-T (mg/kg)</th>
<th>BF3-T (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony (Sb)</td>
<td>0.32</td>
<td>0.94</td>
<td>0.044</td>
<td>1</td>
<td>0.46</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.9</td>
<td>0.1</td>
<td>0.45</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>22</td>
<td>2.7</td>
<td>2.7</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.04</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>0.63</td>
<td>3.3</td>
<td>3.5</td>
<td>1.9</td>
<td>7.5</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>0.54</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.9</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>0.02</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>2.3</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>1</td>
<td>0.2</td>
<td>0.7</td>
<td>0.22</td>
<td>0.36</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>0.44</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>0.15</td>
<td>0.039</td>
<td>0.04</td>
<td>0.039</td>
<td>0.08</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>0.4</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>1.8</td>
<td>0.36</td>
<td>0.12</td>
<td>0.29</td>
<td>0.18</td>
</tr>
<tr>
<td>Zink (Zn)</td>
<td>4.5</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Bromide (Br⁻)</td>
<td>20</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2.1</td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>616</td>
<td>38</td>
<td>84</td>
<td>56</td>
<td>180</td>
</tr>
<tr>
<td>Fluoride (F⁻)</td>
<td>55</td>
<td>3.2</td>
<td>2</td>
<td>12</td>
<td>4.6</td>
</tr>
<tr>
<td>Sulphate (SO₄²⁻)</td>
<td>2430</td>
<td>4200</td>
<td>5900</td>
<td>5700</td>
<td>14000</td>
</tr>
</tbody>
</table>

7.4.4 Pilot test

In addition to the previous laboratory-scale experiments, a larger scale washing experiment was performed. This pilot scale experiment was designed to simulate a real life industrial washing process, such as the industrial mineral washing plant of Van Gansewinkel Minerals. This experimental approach provides vital information on the feasibility and boundary conditions needed, putting this scientific washing approach in practice. The main goals of this pilot study were: firstly, to get better visual and technical indications of a washing process and secondly, to obtain more know-how on the effects of the treatment on the environmental properties of the bioenergy fly ashes.

The experiments were conducted on BF2 and BF3 biomass fly ashes. By testing both types, a broader range of technical treatment properties related to various ash types was conducted. In addition, the individual performance of various treatment steps are analysed, simulating a step-wise real life treatment process.

The ashes were treated within various steps:

*Step 1: Cycloning*

Around 5 kg dry fly ash is mixed for 10 minutes with 50 litres tap water and further treated with a hydrocyclone, with a size separation dimension of 63 µm. In one session both cyclonated fractions were sampled (top and bottom flow). The top fraction ≤ 63 µm
contained the very fine particles and the overall initial organic carbon fraction. The bottom fraction $\geq 63 \text{ µm}$ is the inorganic content (78% dry matter) and was used as input for the flotation step; the two biomass fly ashes obtained are termed BF2-C and BF3-C.

**Step 2: Flotation**

The input cycloned fraction $\geq 63 \text{ µm}$ BF2-C was diluted with tap water up to 35% dry matter, in a total volume of 1 litre. Firstly, for 10 min. the mixture was conditioned (slowly mixed) with a small addition (drops) of collector (liquid soap), which acts as complexion polymer toward potential contaminates like heavy metals, mineral oil and polyaromatic hydrocarbons. The mechanism behind complexion is based on a reactive negatively charged hydroxyl group, which forms a complex with cationic species (Figure 7.11). In addition, this contaminant-complex also contains hydrophobic properties. Secondly, a foaming agent (0.05 ml), which introduces stable air bubbles in the mixture is added and flotation is started (Figure 7.12). The hydrophobic state contaminant-complex is connected to air bubbles and rises in the mixture (together with the leftover organic carbon particles), forming a debris layer which can be extracted and thus creating a contaminant-free mineral fraction. Only the fine bio-fly ash was used for this step, termed BF2-C/F.

**Step 3: Water rinsing**

The fly ash BF2-C/F obtained after flotation was rinsed using tap water, flushing the remaining contaminates out. Within this treatment easy soluble salts (bromide, fluoride, chloride and sulphate) and potential cationic heavy metals were removed (copper, lead, zinc and chromium). The obtained fly ash is termed BF2-C/F/W.

**Leaching results**

All fractions created within the 3 treatment steps were analysed using a cascade test (L/S 10). The leaching results of all obtained treated fly ashes can be seen in Table 7.10. Just as the results from the lab-scale tests (Table 7.9), all obtained fractions have a higher Cr leaching level than accepted; the same case applies for sulphates, but these were reduced in the case of the BF2 treatments. Moreover, antimony has been successfully removed with the pilot treatment steps. In the case of BF2-C the lead leaching is above the limit, but after the following treatment steps this is no longer the case.
Soap collector molecule (negatively charged)

**Figure 7.11:** Complexation mechanism during the cycloning stage of the pilot treatment.

**Figure 7.12:** Flotation scheme (Step 2 of the pilot treatment for BF2).
Table 7.10: Results of the column leaching test on the treated bio fly ashes after the pilot treatment (L/S = 10); bold values exceed the limits set by the Soil Quality Decree (2013).

<table>
<thead>
<tr>
<th>Element/Ion</th>
<th>BF2-C (mg/kg)</th>
<th>BF2-C/F (mg/kg)</th>
<th>BF2-C/F/W (mg/kg)</th>
<th>BF3-C (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony (Sb)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Barium (Ba)</td>
<td>5.5</td>
<td>5.6</td>
<td>6.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Cadmium (Cd)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td><strong>4.8</strong></td>
<td><strong>4.4</strong></td>
<td><strong>4.3</strong></td>
<td><strong>1.5</strong></td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Mercury (Hg)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td><strong>5.2</strong></td>
<td>2.2</td>
<td>1.3</td>
<td>0.26</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>0.29</td>
<td>0.28</td>
<td>0.25</td>
<td>0.64</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Zink (Zn)</td>
<td>1.4</td>
<td>0.52</td>
<td>0.34</td>
<td>0.2</td>
</tr>
<tr>
<td>Bromide (Br⁻)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Chloride (Cl⁻)</td>
<td>110</td>
<td>56</td>
<td>39</td>
<td>400</td>
</tr>
<tr>
<td>Fluoride (F⁻)</td>
<td>7</td>
<td>5.6</td>
<td>4.5</td>
<td>4</td>
</tr>
<tr>
<td>Sulphate (SO₄²⁻)</td>
<td><strong>2220</strong></td>
<td><strong>2180</strong></td>
<td><strong>1970</strong></td>
<td><strong>13000</strong></td>
</tr>
</tbody>
</table>

7.4.5 Economic feasibility

In case a non-hazardous biomass fly ash fulfils the Landfill Ban Decree (2012), the price for landfilling is approximately 40 €/ton; this is exclusive tax of the country (e.g. for the Netherlands this would amount to ±13 €/ton) (Wiebes, 2014). A more favourable situation would be the application of biomass fly ashes in the concrete industry. In case additional treatment is required, like washing and separation, the price will increase with approx. 20 €/ton. If the material is too coarse and requires milling, the cost increase would be approx. 10-15 €/ton (+1 €/ % moisture content for drying if it cannot be used wet, all costs without tax). Additional costs like storage and analyses will be ±3 €/ton, while the residue (sludge) will be sent to a landfill, at a cost of approx. 8 €/ton of sludge excluding tax. This residue (accumulated with metals and salts) needs to go to landfill and depending on the type of fly ash e.g. the carbon content and fine fraction (≤10-20 µm) this will be approximately 15-20% per ton of the initial input material. In this mass percentage the ± 50% water absorption by the material is included.

Finally, two scenarios are possible, namely fly ash treatment (a) without grinding and (b) with grinding which will yield the following costs:

(a) 31 €/ton treatment costs. Indicative market cost is -5 to -10 €/ton (yielding to +4 to -1 €);
(b) 41-46 €/ton treatment costs. Indicative market price is 5 €/ton (yielding to +4 to -1 €). Hence, the approach mentioned in this paper is applicable in practice, allowing biomass fly ashes to enter the market, while having environmentally but also technically an advantage compared to landfilling.
7.5 Conclusions

Although WWCB that did not decay in time are finding its reuse by re-entering the market as a B-product, the potential recycling by reusing in new WWCB is still uncommon. Therefore, the product mostly ends up as demolition waste and together with other organic products get incinerated. To close the loop, a study is conducted on four types of biomass fly ashes to make them suitable to be used as a filler or cement replacer in newly produced WWCB or concrete mixtures. For this the materials were characterised and treatments were performed on both lab-scale and pilot scale, and analysis was done before and after treatment. Based on this, the following conclusions can be drawn:

- Chlorides were found to be the main contaminant from leaching tests, together with sulphates, antimony, chromium and lead. A washing treatment was designed and optimized in terms of duration and L/S ratio in order to remove chlorides efficiently. Besides removing these soluble chlorides, the unburnt carbon content in the grill oven biomass fly ashes was found to be related to their chloride content; a treatment that removed most of the unburnt coal (such as sieving, air filtering and thermal treatments) also lowered significantly the chloride leaching of these fly ashes.

- A pilot test employing cycloning and flotation steps was successfully designed for the upscaling of the proposed treatment. This industrial scale treatment was found to be very efficient for the removal of chlorides, sulphates and chromium (by 99.5%, 90.1% and 72% respectively in the case of BF2).

- The filter ash from a CFB was found to have the highest chloride content; despite the efficiency of the treatments, which lowered the chloride content with ~75%, this particular fly ash is deemed unsuitable for reuse due to its high remaining chloride content. All other fly ashes, either through laboratory treatments or pilot scale treatment were rendered non-hazardous.

- The treatment towards application of the biomass fly ashes, even when milling and washing are required, is environmentally and cost favourable compared to landfilling the material. After treatment, all materials fulfil the legislation and can be utilized.
Chapter 8

Conclusions and recommendations

This chapter provides the main conclusions drawn from the performed study.

8.1.1 Introduction

Wood wool cement boards (WWCB) are boards made of cement, wood wool and water. However, during production, many factors including storage conditions, used knives, recipes and material dosage, influence their properties. In general, moisture is in all stages a very influential parameter, starting from the moisture content \( (Mc) \) of the wood logs. It influences not only the lifetime of cutting knives and energy consumption of the wood wool strands shredding machines but also the dimensions of the produced wood wool strands. Therefore, it is recommended that the \( Mc \) of the wood-logs for board production is between 20-35% based on oven-dry wood. For the cement hydration, proper amount of water is of high importance, to obtain boards that can properly harden. The total water demand required for WWCB during the industrial production can be divided into: (1) the moisture to reach the saturation point of the used wood (30% of the dry oven mass); (2) the outer surface area of the wood wool strands (depending on the dimensions of the wood wool strands); (3) the water demand required to let cement fully react (25% of the mass of cement); (4) the water demand to cover the surface of the cement particles.

8.1.2 Hydration kinetics of cement containing sugars

Since sugars can leach from wood wool and retard cement hydration, the retardation on both white and grey cements with modified CaSO\(_4\) content using glucose was investigated in Chapter 2. It was found that the dosage of CaSO\(_4\) played a very sensitive role on the hydration of cement containing glucose. For grey Portland cement, a slight reduction of CaSO\(_4\) content to 4% already caused a flash set and a dramatic retardation. An increase of the CaSO\(_4\) content to 7% lead to an increased heat release as well as compressive strength. In contrast, for white Portland cement, the reduction of CaSO\(_4\) to 4% resulted in an increased heat release and compressive strength. It was found that in a cement system containing glucose, the production of calcium aluminate hydrates (permeable layer) contributed to a reduced retardation, while calcium aluminate ferrite hydrates (impermeable layer) caused retardation. Furthermore, calcium sulfoaluminate hydrates (impermeable layer) caused retardation, while calcium sulfoaluminoferrite hydrates (permeable layer) did not.

8.1.3 Design of alternative binders for wood composites

To reduce the environmental footprint of WWCB by reducing the cement content, the application of paper sludge fly ash (PsFA) as supplementary lightweight material was studied in Chapter 3. Before PsFA could be successfully utilized, the material required a treatment method due to its large surface area, internal pore structure and free lime content which lead to a high water demand. This together with the water demand of the wood lead to unsuccessful hardening of the remaining binder when cement was replaced...
by 10% by mass. By applying a water amount of 25% by mass of PsFA to powder the free lime content, final surface area and internal pore structure reduced enabling higher replacement levels. After the treatment the replacement of the reference binder used for WWCB by 20% lead to a similar flexural strength of 3 MPa with an apparent density of 470 kg/m$^3$. When applying 60% PsFA-w as cement replacement superior flexural strength was obtained (4.3 MPa with an apparent density of 450 kg/m$^3$). Replacement of the reference binder used for WWCB by 20% reduced the board density with 50 kg/m$^3$ and lowered the thermal conductivity up to 11.8%. When applying 60% of the treated PsFA as cement replacement, a low density board of 400 kg/m$^3$ with the reduced thermal conductivity up to 17.6% was achieved.

Afterwards a second study was performed to design a matrix with lower amount of voids by optimizing the theoretical particle packing density of the binder with the aim to increase the mechanical performance of the board and to reduce the amount of cement. It was found that the modified Andreasen and Andersen model works also to optimize the binder layer of wood wool cement boards (Chapter 3). By applying an optimized particle packing, substitution of cement by 70% mass of binder could be achieved by using a hydraulic binder (20%) and fillers (50%).

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

Another investigated method to reduce the environmental footprint of WWCB was to replace cement by alkali activated binders (Chapter 4). However, this required first fundamental understanding of the interaction between alkalis and wood since wood wool is able to neutralize 53% of the initial OH$^-$ ions leading to a reduction of the pH from ~13 to ~12.6. Hence, reactivity of alkali activated binder was negatively affected. It was found that the ionic uptake of wood resulted in insufficient reaction of the alkali-activated binder but could be compensated by additional OH$^-$ and Ca$^{2+}$ ions from an alkali pre-treatment or substitution of the alkali activated binder by cement. However, also the initial $M_c$ of the wood wool had a strong influence on whether alkali activated binders properly harden or not. Because a high water demand lead to a diluting effect while a low amount of water lead to increased movement of water and ions to the wood wool due to the wood wool hydroscopic properties. The NMR results indicated that an addition of 60% water on dry mass of wood was sufficient to pre-treat the wood wool, resulting in the highest mechanical properties. Application of 100% alkali-activated binder with proper initial pH or a hybrid binder demonstrated very promising results, especially indicated by a remarkable CO$_2$ footprint reduction by 72.9% and 61.5% respectively compared to a pure cement system.

### 8.1.5 Advanced functionalities

Because of the open structure and rough surface of WWCB, the material was investigated to become an air purifying material, adding an additional feature to this almost century old product. It was found in Chapter 5 that WWCBs had good support properties that allowed the use of very low quantity of TiO$_2$, while realizing a high degradation rate (> 95%). This increases not only the indoor air quality but also makes the application of TiO$_2$ for air purification also more cost efficient. This extraordinary performance was
related to the high surface area while maintaining a high mass transfer due to the open surface structure. The TiO$_2$ particles were homogeneously coated on a wider surface, allowing a greater efficiency, and thus higher degradation amount. Moreover, no intermediate compounds (NO$_2$) were produced from the degradation of NOx. A water treatment indicated the suitability and adhesion of the coating to the substrate while surface analyses indicated that the presence of porosity with depth higher than 4 mm was not able to rise the performance of the coating. It was found that PC provided the best adhesion of the coating on the board, although the coating lost efficiency if applied in early stages of board manufacture.

8.1.6 Modeling and optimization of the sound absorption of wood wool cement boards

The main application of WWCB is as a ceiling material because of its sound absorption properties. In chapter 6, boards with varying strand widths, densities and thickness were acoustically characterized by means of an impedance tube and optimized using an impedance model applying different board densities and boards with a stepwise density. Furthermore, the performance of a board when an air cavity was applied was investigated. It was found that the acoustic impedance of WWCB with low errors can be obtained by using the Johnson-Champoux-Allard (JCA) model. The model uses both measured parameters and parameters derived from measured values in the impedance tube. The porosity can be better derived from the measured values in the impedance tube than measured directly using a pycnometer since not all the voids in the wood wool and more importantly the voids between the wood wool strands do not effectively take part in the sound absorption process. By using the JCA model, it was found that increasing the density from 350 kg/m$^3$ to 550 kg/m$^3$ increased the sound absorption by 44, 14 and 25% for the 1.0, 1.5 and 2.0 mm strand width respectively. Above a density of 650, 700 and 800 kg/m$^3$ for 1.5 mm, 2.0 and 1.0 mm respectively, the sound absorption declined. Application of a multilayer WWCB with a stepwise density showed improved sound absorption in which the first layer should have a lower density compared to the second layer. Finally, when mounting a 25 mm WWCB on a rigidly backed air cavity, a width of 100 mm behind the board lead to the highest sound absorption for all investigated boards.

8.1.7 Disposition after service life and treatment of biomass fly ashes

Although WWCB that did not decay in time are finding its reuse by re-entering the market as a B-product, the potential recycling by reusing shredded boards in new WWCB is still uncommon. Therefore, the product mostly ends up as demolition waste and together with other organic products gets incinerated. To close the loop of material usage, Chapter 7 investigated the potential use of four types of biomass fly ashes to make them suitable to be used as a filler or cement replacer in newly produced WWCB or concrete mixtures. However, since the large volume required for the incineration and the relatively small waste volume of WWCB, the waste is often mixed with B-wood and organic products like dry paper sludge forming biomass. Because of this, the maximum leaching values of the fly ashes to be used as a building material exceeds the limit which requires treatment before reuse. By following a lab scale treatment method of sieving, air filtering, water treating and milling, the leaching values of contaminants like chlorides sulphates, antimony, chromium and lead could be successfully reduced and the material could be
successfully utilized. A pilot test employing cyclone and flotation steps was then successfully designed for the upscaling of the proposed treatment. This industrial scale treatment was found to be very efficient for the removal of chlorides, sulphates and chromium (by 99.5\% , 90.1\% and 72\% respectively in the case of BF2). The treatment towards application of the biomass fly ashes, even when milling and washing are required, is environmentally and cost favourable compared to landfilling the material. After treatment, all materials fulfil the legislation and can be utilized. Replacement of cement up to 40\% without any noticeable effects on the board properties were found. In comparison with limestone powder, the use of biomass fly ashes led to a 10\% increase in mechanical strength since it acts as an active filler.

8.2 Recommendations for future research

The present PhD project was triggered to gain insight in the properties of WWCBs in order to make WWCB more sustainable by replacing cement with eco-friendly materials, broaden its functionality. The above presented results positively indicated the achievements and validity of the performed study. Nevertheless, based on the present study further research is still necessary.

The following work is summarized as the recommendations for future investigations:

1. The wood wool, binder and water ratio’s for different wood wool strand widths and thicknesses, as well as pre-treating the wood and mixing the wood with a slurry instead of dry powder.
2. The suitability of a modified CaSO$_4$ content for white and grey cement using wood types which are classified as highly cement retarding.
3. The synergetic effect of the treated PsFA and secondary cementitious materials (e.g. ground granulated blast furnace slag and fly ash) on cement hydration and final performance of lightweight cement composites, in order to acquire a further reduced CO$_2$ footprint and in the meantime improved properties.
4. Optimization of the sound absorption in the low-frequencies by e.g. implementing mineral wool fibers, different natural fibers or porous binders in WWCB.
5. Durability and sustainability study of wood wool having a photocatalyst implemented to make it air purifying. If the wood wool is degraded in time by the TiO$_2$ presented and how is the long time performance under different (weather) conditions, both indoor and outdoor.
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List of symbols and abbreviations

Abbreviations

AAB Alkali Activated Binders
ATR Attenuated Total Reflection
BET Brunauer-Emmett-Teller
BF1 Boiler fly ash
CSH Calcium Silicate Hydrate
CT Computer Tomography
CFD Computational Fluid Dynamics
EDX Energy-dispersive X-ray spectroscopy
EPS Expanded Polystyrene foam
FSC Forest Stewardship Council
FA Fly Ash
FTIR Fourier Transform Infrared Spectroscopy
G CEM I 52.5 R
GGBFS Ground Granulated Blast Furnace Slag
GWP Global Warming Potential
HB High binder amount
JCA Johnson Champoux Allard
JCAL Johnson Champoux Allard Lafarge
LB Low binder amount
LOI Loss On Ignition
LP Limestone Powder
NMR Nuclear Magnetic Resonance
PC Ordinary Portland Cement
PCO Photocatalytic Oxidation
PEFC Program Endorsement Forest Certification
PF Phenol formaldehyde resin
PIR Polycyanurate
PM Airborne particulate matter
PSD Particle Size Distribution
PsFA Paper sludge Fly Ash
RMSD Road Mean Square Deviation
SA Surface Area
SEM Scanning Electron Microscope
SCM Supplementary cementitious materials
SR Surface Roughness
SSA Specific Surface Area
TGA Thermal Gravimetric Analysis
VOC Volatile Organic Compounds
W CEM I 52.5 R White
W/B Water to Binder ratio
W/P Water to Powder ratio
WHO World Health Organization
WCC Wood Cement Composite
WWCB Wood Wool Cement Board
XPS Extruded Polystyrene
XRF X-ray Fluorescence
XRD X-ray Diffraction
Symbols

Roman

\( \alpha_{model,j} \) absorption coefficient of 1/3 octave band \( j \)
\( \alpha_{\infty} \) tortuosity
\( d \) thickness of the sample \([\text{m}]\)
\( D \) particle size \([\mu\text{m}]\)
\( D_{\text{max}} \) maximum particle size \([\mu\text{m}]\)
\( D_{\text{min}} \) minimum particle size \([\mu\text{m}]\)
\( e^- \) reducing agent
\( G_b \) dimensionless specific gravity of the green volume of wood
\( h^+ \) oxidation agent
\( m_a \) mass which is left after 1 h at 750 °C \([\text{g}]\)
\( M_c \) moisture content of wood \([\%]\)
\( m_{cell} \) mass of oven-dry wood after 24 h at 105 °C \([\text{g}]\)
\( m_i \) mass of impregnated wood \([\text{g}]\)
\( m_p \) mass of the measured powder \([\text{g}]\)
\( m_w \) mass of the applied water \([\text{g}]\)
\( N_{pr} \) Prandtl number \((\approx 1.4)\)
\( P \) packing of a material in the range of 0-1
\( P(D) \) fraction of the total solids being smaller than size \( D \)
\( Q \) volumetric airflow rate passing through the sample \([\text{m}^3/\text{s}]\)
\( q \) distribution modulus
\( r \) sample radius \([\text{m}]\)
\( V_{cell} \) volume of the cell walls \([\text{cm}^3]\)
\( V_p \) volume of the powder \([\text{cm}^3]\)
\( V_{voids} \) void volume of the wood \([\text{cm}^3]\)
\( V_w \) volume of water \([\text{cm}^3]\)
Greek

\( \Delta p \) air pressure difference across the test specimen \([\text{Pa}]\)
\( \gamma \) ratio of the specific heat capacity \((\approx 1.4)\)
\( \eta \) viscosity of air \((\approx 1.84 \times 10^{-5})\) \([\text{kg/(ms)}]\)
\( A \) viscous characteristic length \([\mu\text{m}]\)
\( A’ \) thermal characteristic length \([\mu\text{m}]\)
\( \rho_d \) density of the powder \([\text{g/cm}^3]\)
\( \rho_w \) density of water \([\text{g/cm}^3]\)
\( \rho_0 \) density of air \([\text{kg/m}^3]\)
\( \rho_0c \) representing the impedance of air \([\text{Pa-s/m}]\)
\( P_0 \) atmospheric pressure \((\approx 101,320 \text{ Pa})\) \([\text{Pa}]\)
\( \sigma \) flow resistivity \([\text{Ns/m}^4]\)
\( \phi \) porosity
\( \omega \) angular frequency \([1/\text{s}]\)
Summary

Development of sustainable and functionalized inorganic binder-biofiber composites.

This thesis addresses the performance based design and evaluation of lignocellulosic cement composite boards, which are commercially known as wood wool cement boards (WWCB). The origin of WWCB goes back to around 1920 and is still popular nowadays, because: (1) their lightweight porous structure makes them of interest as a filler providing thermal insulation and sound absorbing properties (2) the applied binding agent cement mineralizes the lignocellulose, adding high resistance to bio-degradation and fire resistance. The boards can be applied as roof and ceiling material or as an exterior wall where a high durability and low maintenance are desired. Despite the advantageous application of cement in lignocellulosic composites, the inhibitory influence of the lignocellulosic components on the cement hydration is well known, which is not desired for this application as for the production cycle a fast setting and hardening of Portland cement (PC) is required. Moreover, the increasing awareness worldwide of the substantial contribution of PC to greenhouse gas emissions results in searching for alternative materials and the development of new binder types.

The thesis starts with an introduction of WWCB explaining its ingredients and the production process and resulted board properties of commercial WWCB. Next, the hydration kinetics of cements is studied and the retardation of sugars on cements with varying aluminate and CaSO₄ contents are evaluated, providing new insights into the retardation mechanism. Based on the acquired knowledge, efficient utilization of binders through approaches including particle packing, modified mixing procedures and implementation of supplementary materials is investigated, leading to new WWCB with increased mechanical and thermal properties and reduced environmental footprints. The use of alkali-activated binders is then studied to fully replace cement, based on the understanding of the alkaline degradation mechanism of wood and reaction mechanisms, which result in the development of a hybrid binder with a reduced a carbon footprint of up to 60% compared to the use of cement as binder and a significant reduction in costs. An orientated study is then performed on increasing the functionality of the boards by implementation of photocatalysis based on the fundamental insights in the surface morphology, which ultimately result in an air purifying WWCB with a high air pollutant degradation efficiency of 98%, emphasizing the coatings durability. Since one of the main WWCB properties is sound absorption, a study is performed to characterize and to predict the sound absorption of WWCB with varying strand widths, densities, thicknesses and air cavities, by using impedance models. Moreover, the sound absorbing properties are further optimized by modifying the densities and construction structure. Finally, the disposal of commercial WWCB after its service life time is considered, leading to waste wood incineration and contamination of residues that required the design of economical feasible treatments which in the end are verified on a pilot scale, resulting in a binder which could be re-used as a supplementary material of cement.
List of publications

Publications on the performed work and joined projects during this PhD.

**ISI Journals**


**Conference proceedings**


Curriculum Vitae

Education

2012 – 2018: Ph.D at Building Materials
Thesis title: “Development of sustainable and functionalized inorganic binder-biofiber composites”
Eindhoven University of Technology, Department of The Built Environment
Eindhoven, The Netherlands
2010 – 2012: MSc. in Building Physics
Thesis title: “Physical and chemical upgrading of bio-energy fly ash from incineration of wood”
Eindhoven University of Technology, Department of The Built Environment
Eindhoven, The Netherlands
2007 – 2010: BBE. in Civil Engineering
Avans Hogeschool (HBO), Academy of Building Construction and Infrastructure
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Professional Experience

Eindhoven University of Technology, Department of The Built Environment
Objectives:
- implementation of eco-friendly binders,
- reduction of inhibitory effect of wood,
- modeling of acoustical properties of wood wool cement boards,
- evaluation of moisture influence on board performance

ROC de Leijgraaf
Objectives:
- Teaching building technology specialized in building physics and sustainable buildings,
- Development of education programs, quality improvement and funding for a new education program involving companies.

April. 2018 – to present: Project leader Research and Development
Ascem part of Bouw Toeleveringsindustrie Europa (BTE)
Objectives:
- Optimization of existing product catalogues, creation of technical documentation,
- Development of new prefab concrete products.

Feb, 2014 – 2015: Project leader
Eindhoven University of Technology, Department of The Built Environment
Project title: “Development of a solar energy collecting roof with natural aesthetics and orientation independence [3TU Leafroof project]”
Objectives:
- Design of a roof tile from luminescent solar concentrating (LSC) material,
- Implementation of PV solar cells to the tiles,
- Optimization of the product (incl. protective films and coatings.

Sep, 2011 – Aug, 2012: internship as a part of graduation project (M.Sc.)
Van Gansewinkel Minerals and Eindhoven University of Technology, Eindhoven (NL)
Project title: “Physical and chemical upgrading of bio-energy fly ash from incineration of wood”
Results:
- Proposal and evaluation of treatment techniques,
- Feasibility tests (laboratory scale) and practical/industrial application.

Sep, 2008 – Aug, 2010: Project engineer
Nieman Consultancy, Eindhoven (NL)
Consultant in building physics for residential and non-residential buildings
Tasks:
- Evaluation of building physics issues in construction projects related to natural light, ventilation, fire safety, building regulations, acoustics, energy and performance,
- Integral advice on building physics and architectural (construction) design.
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Development of sustainable and functionalyzed inorganic binder-biofiber composites  
Guillaume Doudart de la Grée
This thesis addresses the performance-based design and evaluation of lignocellulosic cement composite boards, which are commercially known as wood wool cement boards (WWCB). The origin of WWCB goes back to around 1920 and is still popular nowadays. This thesis starts with an introduction of WWCB by explaining its ingredients and the production process. Next, the retardation of sugars on cements is evaluated, providing new insights into the retardation mechanism when combining wood and cement. To reduce the environmental footprint of the boards, implementation of supplementary materials and the use of alkali-activated binders are studied. An oriented study is then performed on increasing the functionality of the boards by making it air purifying using the fundamental insights in the surface morphology. Since one of the main WWCB properties is sound absorption, a study is performed to characterize and to predict the sound absorption of WWCB by using impedance models. Finally, the disposal of commercial WWCB after its service lifetime is considered, leading to waste wood incineration and contamination of residues that require the design of economical feasible treatments.