Construction and Building Materials 143 (2017) 48-60

Contents lists available at ScienceDirect



Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Assessing the effect of CaSO₄ content on the hydration kinetics, microstructure and mechanical properties of cements containing sugars



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HIGHLIGHTS

- The effect of sugar on cement hydration kinetics and microstructure is studied.
- The effect of CaSO₄ on cement hydration containing sugars is studied.
- The relation between CaSO₄ and cement composition on cement hydration is studied.
- An optimal CaSO₄ content is found for cements containing sugars to reduce retardation.
- Wood cement composites were designed to successfully validate the present findings.

ARTICLE INFO

Article history: Received 2 November 2016 Received in revised form 17 February 2017 Accepted 9 March 2017

Keywords: Cement Hydration kinetics Sugar CaSO₄ Heat release Aluminate ferrite hydrates Hydration products

ABSTRACT

This article aims to study the hydration kinetics of cements containing sugars. The effects of Portland cement constituents (including aluminate and ferrite phases and CaSO₄ content), and a sugar (glucose) on the hydration kinetics, microstructure and mechanical properties, were evaluated. The heat release during the hydration was analysed using an isothermal calorimeter. The reaction's products, gel structure and microstructure at different hydration times were analysed by the analytical methods XRD, FTIR and SEM. Furthermore, mortars and wood-wool cement composites were designed to validate the present findings. It is concluded that the newly derived binder can overcome retarding effects and result in wood-wool cement composites with excellent performance.

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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 [1,2], the utilisation of by-products containing organics to partially replace cement [3,4], the application of organic fibres in concrete [5], and the use of retarding admixtures in concrete [6–8]. In the case of admixtures, the retardation leads to a favourable condition by delaying the setting time of the cement [9–12]. 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 Na₂SiO₃ or CaCL₂ are added [13], although the latter is restricted to wood cement composite boards [14,15].

Studies have been extensively conducted in the last centuries on the retarding mechanism of organic admixtures on Portland cement [6,8,11,16-25]. 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 [21]. 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 [16]. 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 [23], mainly acids [26,27], capable of forming complexes with cations by acting as a ligand. This consequently favours the Ca [25], Al, and Fe chelating complexations [16,21] that arise with organic compounds containing one or more oxy-functional groups [28]. 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 [24] and (2) forming insoluble metal organic complexes, which coat the clinker phases [29]. 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 Fig. 1.

Numerous researches have investigated the effects of organic compounds on the setting and early hydration of various cement phases, including C₃A since it is the fastest reacting phase and C₃S since it is the phase that dominates the early strength development [16]. In the presence of C₃S, the effect of C₃A is the removal of the admixture from the solution, thereby preventing a strong retarding effect on C₃S [16]. Cheung et al. [12] reported the importance of supplying sulphate 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 [30,31]. 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 C₃S 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 [15,32]. 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 the observed reactions could be more easily interpreted. Moreover, glucose in concentrations of 0.05–0.3% is often used [11,16,19,22,24,12,33] in cement chemistry and wood cement composite science research [34,35] because of its retardation mechanism.

The effect of the CaSO₄ 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% CaSO₄ and white cement with 4% CaSO₄ content.

2. Materials and methods

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 (grey) 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 [36,37], are presented in Table 1.



Fig. 1. Schematic overview of the inhibitory effect of glucose on cement hydration. A) dissolution of cement particles; B) ring opening of glucose and complexation of metal ions; C) formation of acids and salts precipitating on the surface of cement.

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 N₂ adsorption, a Malvern Mastersizer 2000, and an AccuPyc 1340 II gas Pycnometer, respectively. *G* has a BET surface area of 1.50 m²/g, a mean particle size d₅₀ of 14.44 μ m, and a specific density of 3150 kg/m³, whereas *W* is a bit coarser with a BET surface area of 1.21 m²/g, a mean particle size d₅₀ of 16.90 μ m, and a specific density of 3106 kg/m³. Compared to *G*, *W* has a higher C₃A content (~3%) and a higher C₃S content (~ 20%), while having a similar gypsum content (both ~ 3%).

D-glucose (Merck KGaA) was used in the present study. Two different dosages of 0.2 and 0.3% by mass of cement, corresponding to a $(C_3A + C_4AF)$ /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 composites (WWCC) 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 woodwool [38] and, therefore, a potentially large influence on the binder hydration mechanism. Secondly, during the production process of WWCC, 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 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/m³ and 1345 kg/m³, 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 [39], and the acid soluble lignin according to Tappi UM250 [40]. The extractives were determined according to Tappi T264 [41]. The polysaccharides, hemicelluloses, and cellulose were determined by acid hydrolysis using a high performance anion exchange chromatograph (HPAEC). Table 2 presents the chemical composition of the wood. Glucose is the major sugar, along with Arabinose, Xylose, Rabmnose, Mannose, and Galactose. Reported literature indicated a slightly higher glucose content ranging between 41.5 [42] and 45.5 [43] 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 [25]. This reflects the validity of using glucose as a representative to study the cement hydration kinetics containing wood.

2.2. Experiments

To study the hydration kinetics, a series of mixtures listed in Table 3 were tested by using a TAM AIR isothermal calorimeter. The heat release was recorded for 90 h with a water to powder

Table	1

Chemical composition and main compounds.

Tahl	e 7	

Chemical composition of the used spruce wood in [%].

Compound	[%]
Cellulose Glucose	38.7
Hemicellulose Arabinose	1.3
Xylose Rhamnose Mannose	5.6 0.4 11.5
Galactose Galacturonic acid	2.6 1.1
Glucuronic acid	1.9
Lignin (according to TAPPI T222 and TAPPI U. Acid insoluble lignin Acid soluble lignin	M250) 25.4 0.2
Extractives (according to Tappi T264) Cyclohexane: Ethanol 2:1 Ethanol: Water 1:1 Water	1.8 1.3 1.6

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 [44–46]. Minor mass loss due to the loss of the chemically bound water in CSH in this range was neglected [47]. 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.

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), 4000–400 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 $40 \times 40 \times 160 \text{ mm}^3$ and vibrated. Finally, all specimens

Chemical composition	G [%]	W [%]	Phases	G [%]	W [%]
CaO	63.71	67.19	C₃S	56	80
SiO ₂	20.27	20.86	C ₂ S	17	0
Al ₂ O ₃	4.80	3.91	C ₃ A	7	10
Fe ₂ O ₃	3.43	0.45	C ₄ AF	10	1
SO ₃	2.91	2.92	CS	5	5

Table 3	3	
Tested	reci	pes.

Mix	Variables		Ratios		
	Portland cement type	Glucose (wt.% cement)	CaSO ₄ (wt.% cement)	Glucose/($C_3A + C_4AF$) [%]	$CaSO_4/(C_3A + C_4AF)[-]$
1	G	0	5.0	0	0.294
2	G	0	-	0	-
3	G	0.2	5.0	1.17	0.294
4	G	0.2	-	1.17	-
5	G	0	4.0	0	0.235
6	G	0.2	4.0	1.17	0.235
7	G	0	2.5	0	0.147
8	G	0.2	2.5	1.17	0.147
9	G	0.2	6.0	1.17	0.353
10	G	0.2	7.0	1.17	0.412
11	G	0.3	5.0	1.76	0.294
12	G	0.3	4.0	1.76	0.235
13	G	0.3	6.0	1.76	0.353
14	W	0	5.0	0	0.455
15	W	0	-	0	-
16	W	0.2	5.0	1.81	0.455
17	W	0.2	-	1.81	-
18	W	0	4.0	0	0.364
19	W	0.2	4.0	1.81	0.364
20	W	0	2.5	0	0.227
21	W	0.2	2.5	1.81	0.227
22	W	0.3	5.0	2.72	0.455
23	W	0.3	4.0	2.72	0.364

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 [48].

The WWCC were produced using the following recipe and preparation procedure. A total water to powder ratio of 1.0 by mass of cement and a wood to powder ratio of 0.75 by mass of cement was used [38]. The target density of the boards was 450 kg/m^3 . 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 s. Next, the wood-wool cement composite was transferred into a mould with a size of 30×50 cm² (W × 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 15×20 cm² (W × 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 [49].

3. Results and discussions

3.1. Hydration kinetics of cements/clinkers without glucose

Fig. 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 Fig. 2b. The first sharp peak was attributed to the dissolution of particles and fast reaction of C₃A that reacts with Ca²⁺ and SO₄²⁻ ions, yielding the formation of calcium sulfo aluminate hydrates in the form of (Ca₆Al₃(-SO₄)₃(OH)₁₂, ₂₆H₂O) [7] and hydroxy–AFm [50]. 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 [7]. The hydration of C₃A with gypsum and water formed calcium sulfoaluminate hydrate, ettringite, reading:

$$C_3A + 3C\bar{S}H_2 + 26H \rightarrow C_6A\bar{S}_3H_{32} \tag{1}$$

When all the gypsum in the cement was consumed by the reaction with C_3A , the remaining C_3A dissolved until the solution becomes supersaturated with respect to calcium aluminate monosulfate, which then precipitated together with other amorphous phases [51,52].

 C_3S reacted in the pre-induction period in small quantities, yielding CSH gels and contributed together with the C₂S 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 SO_4^{2-} 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 C_3A (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 [51]. The higher the gypsum content, the longer it takes for the gypsum to be fully consumed and the later the third peak occurs [51,53]. The reaction of C₄AF was essentially similar to that of C_3A [54] in the presence of SO_4^{2-} 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) [52,55].

The thermal analysis presented in Fig. 3 displays an increasing amount of portlandite in the early age reaction (20,72 h) which is attributed to the reaction of C₃S, following [9]:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \tag{2}$$

However, according to Taylor [7], the hydration of C_3A in time is to a high degree delayed by the reaction with $CaSO_4$, and it is also delayed in the presence of a high quantity of portlandite. Therefore, consumption of portlandite occurs by the reaction of C_3A [7,24,56], as:

$$C_3A + CH + 18H \rightarrow C_4AH_{19} \tag{3}$$

and in case C₄AF [9], as:

$$C_4AF + 2CH + 10H \rightarrow C_3AH_6 + C_3FH_6 \tag{4}$$



Fig. 2. (a) Normalized heat, and (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).



Fig. 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% CaSO₄ (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% CaSO₄ (7.5 and Mix 8.0 J/g), as presented in Fig. 2. This is mainly due to the reaction of C₃A forming calcium aluminate hydrates. The difference in the heat release between G and W is related to the higher quantity of C₃A present in W. The heat release of Mix 2 rapidly increased for 9 h, which is attributed to the reaction of aluminate phases C₃A and C₄AF. The results indicate that the reaction continued and was not retarded by the hydration products covering the cement particles. Taylor [7] mentioned a similar behaviour, stating that the reaction of C₄AF in the presence of high amounts of portlandite can be slowed down. Mix 15 showed, after the preinduction period, a gradual increase of heat up to 24 h, and no third peak was observed due to the absence of CaSO₄. The initial increase of heat is attributed to the reaction products from C₃A corresponding to the phases C_2AH_x and C_4AH_x that ultimately converted to a more stable hydrate C_3AH_x [7]. Because of the reaction of C_3A and initial dissolution of C₃S that precipitates on the cement particle surface, the cement hydration was retarded [7]. Therefore, in the case of no $CaSO_4$ being present, the higher the C_3A content, the more reaction products precipitated on the cement particles, increasing the retardation.

The analysis in Fig. 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 C_3S or lower consumption of portlandite by the reaction of C_3A and C_4AF . The fast hydration of C_3A lead to a lesser formation of portlandite, but in time the amount of portlandite increased due to the reaction of C_3S . The greater amount of C_3S in *W* compared to *G* caused the deviation in the amount of portlandite between the samples. The XRD analysis presented in Figs. 4 and 5 confirms the presence of crystalline portlandite in both Mix 1 and Mix 14 and Mix 2, and Mix 15 at 20 h and 72 h.

3.2. Hydration kinetics of cements/clinkers containing glucose

The heat evolution and heat flow rate of the cements were significantly altered when glucose ($C_3A + C_4AF/glucose$ ratio 1.17% for *G* and 1.81% for *W*) was added to the mixtures, as presented in Fig. 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 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 C₄AF, which with a w/b ratio of 0.4, has an enthalpy of 289 J/g after 3 days of hydration [7], while W contains almost no C₄AF. In G, C₄AF reacted in the presence of portlandite and CaSO₄, slowly forming AFt that later was transformed to AFm, preventing a flash set similar to C₃A. Furthermore, the reaction of C₃A with CaSO₄ and glucose lead to a thin and impermeable layer of AFt [24]. In Mix 16, the reaction of C₃S continued, observed by the strength development (as will be discussed in Section 3.5), although indicated by a low heat release (enthalpy of 243 J/g [7]). This was confirmed by the enlargement of the heat release, indicating the main reaction starting from 14 h (Fig. 6). Therefore, the high heat release of Mix 3 is attributed to the C₄AF reaction, since the other reacting compounds C₃A and C₃S present in W release a low amount of heat. This is further explained by the heat release of G with 0% CaSO₄ and glucose (Mix 4) and W with 0% CaSO₄ and glucose (Mix 17).

It was clearly demonstrated from the heat releases of Mix 4 and Mix 17 that C₃A 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



Fig. 4. XRD pattern showing the main portlandite peaks (at 2Θ of 18 and 34) for G with 5% CaSO₄ (Mix 1) and W with 5% CaSO₄ (Mix 14) at 0, 20 and 72 h of hydration.

example, in the case of Mix 4, retardation beyond 90 h was observed due to the lower content of $CaSO_4$ and a reduced reaction of C_3S . In the presence of $CaSO_4$, C_4AF formed calcium sulfoferrite hydrates as well as calcium sulfoaluminate hydrates [52], as

$$C_4AF + xCS + yH \rightarrow C_4 S(A_{0.75}, F_{0.25})H_{(y-4)} + 0.75FH_3 + CH + 0.25AH_3$$
(5)

Its presence accelerates the hydration of the silicates [57]. In the absence of $CaSO_4$ and increased dissolution of C_4AF 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 C_3S [24]. Together with the fast reaction of C_3A , a fast stiffening of the paste resulted. Furthermore, the amounts of C_3A and C_4AF in *G* exceed the amount of C_3A in *W*, resulting in more products precipitated on the other cement compounds. This is supported by the present findings that Mix 16 (containing no C_4AF) 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 Fig. 7 containing glucose to the results presented in Fig. 3 without glucose, it is clear that the



Fig. 5. XRD pattern showing the main portlandite peaks (at 2Θ of 18 and 34) for G with 0% CaSO₄ (Mix 2) and W with 0% CaSO₄ (Mix 15) at 0, 20 and 72 h of hydration.

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 Figs. 8 and 9 confirm a decrease in crystalline portlandite compared to the mixtures without glucose.

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 3.5.

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



Fig. 6. (a) Normalized heat, and (b) Normalized heat flow of 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).



Fig. 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.

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 Fig. 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.

When the CaSO₄ was reduced in *W* to 4% (Mix 18), the main reactions of C_3S and C_3A were accelerated because of the reduced CaSO₄ amount, and the amount of CaSO₄ present started to be quickly consumed by C_3A . Therefore, the third reaction peak that normally occurs at 18 h after CaSO₄ is depleted, occurred at 10 h. Similar results were reported on pure C_3A using various amounts of CaSO₄ [50]. Furthermore, while *W* with 5% CaSO₄ and glucose (Mix 16) was retarded until 43 h (Fig. 6), *W* with 4% CaSO₄ and glucose (Mix 19) was only retarded until 20 h (Fig. 10). Because of the incorporation of glucose in the reaction products of C_3A , less glucose was available to retard C_3S .



Fig. 8. XRD pattern showing the main portlandite peaks (at 2Θ of 18 and 34) for G with 0.2% glucose and 5% CaSO₄ (Mix 3) and W with 0.2% glucose and 5% CaSO₄ (Mix 16) at 0, 20 and 72 h of hydration.

In the presence of glucose, the hydration of C_3A 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 release of Mix 16. The second C_3A 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 interlaminar region [58] which is confirmed by



Fig. 9. XRD pattern showing the main portlandite peaks (at 2Θ of 18 and 34) for G with 0.2% glucose and 0% CaSO4 (Mix 4) and W with 0.2% glucose and 0% CaSO₄ (Mix 17) at 0, 20 and 72 h of hydration.

Young [59]. The reduced peak height indicates that the amount of calcium sulfoaluminate hydrates is reduced, which is able to react with C₃A. The positive reaction mechanism to reduce the influence of glucose was also observed by the SEM analysis and in accordance with the high heat liberation in time. Additional tests using FTIR presented in Fig. 11 indicate the presence of CSH gel at about 950 cm⁻¹ [60] for both *W* and *G* samples, with adjusted CaSO₄ 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.

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 [24] 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 C_4AH_x from C_3A [20] and C_4FH_x from C_4AF 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 [24]. 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 [52] derived from the reaction of C₄AF (Fig. 12a). This, while increasing the CaSO₄, lead to an increment of calcium sulfoaluminoferrite phases [52] that allowed the continuous reaction of the cement (Fig. 12b). For W, a reduction inCaSO₄ lead to an increased production of calcium aluminate phases (Fig. 12c), which in turn allowed the further reaction of cement due to their different stacking (Fig. 12d). 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.

3.4. Effect of glucose content

In case of a higher glucose content e.g. $glucose/(C_3A + C_4AF)$ mass ratio of 1.76% for *G* and 2.72% for *W*, as presented in Fig. 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/ $(C_3A + C_4AF)$ 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 CaSO₄ 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 CaSO₄ content, the initial heat release increased, indicating a higher dissolution and more glucose forms, acids, and complexations with the C₃A products.

Collepardi et al. [22] 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 [20], 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 h. This shows that both systems react differently, attributed to the presence/absence of ferrite phases. The amount of glucose seemed to change the reaction



Fig. 10. (a) Normalized heat and (b) Normalized heat flow of G with 0.2% glucose and 4% CaSO₄ (Mix 6), G with 0.2% glucose and 6% CaSO₄ (Mix 9) and W with 0.2% glucose and 4% CaSO₄ (Mix 19); (c) Normalized heat and (d) Normalized heat flow of G with 0.2% glucose and 2.5% CaSO₄ (Mix 8), G with 0.2% glucose and 7% CaSO₄ (Mix 10), and W with 0.2% glucose and 2.5% CaSO₄ (Mix 21).



Fig. 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) and (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).

of *W* since a continuous liberation of heat was not observed with lower glucose concentrations or when using grey cement.

3.5. Mechanical properties of mortars and wood-cement composites

From the strength results presented in Fig. 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_3S 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



Fig. 12. Reaction mechanism in the presence of glucose forming permeable and impermeable layers of hydration products.



Fig. 13. (a) Normalized heat, and (b) Normalized heat flow of G with 0.3% glucose and 5% CaSO₄ (Mix 11), G with 0.3% glucose and 6% CaSO₄ (Mix 13), W with 0.3% glucose and 5% CaSO₄ (Mix 22) and W with 0.3% glucose and 4% CaSO₄ (Mix 23).



Fig. 14. (a) Flexural strength and (b) Compressive strength of mortars 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), 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).



(b)



Fig. 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) and (d) W with 0.2% glucose and 4% CaSO₄ (Mix 19).

Table 4	
Evaluated WWCB with their density and flexural	strength properties.

Boards [*]	CaSO ₄ (wt.% cement)	Wood/water [-]	Wood/powder [-]	Density [kg/m ³]	Flexural strength [MPa]
C_WWCC	5.0	0.75	1.0	399.1	1.9
C_WWCC	5.0	0.75	1.0	455.7	3.0
C_WWCC	5.0	0.75	1.0	570.5	4.9
Mix 1	5.0	0.75	1.0	580	3.8
Mix 1	5.0	0.75	1.0	451	2.4
Mix 1	5.0	0.75	1.0	364	1.3
Mix 10	7.0	0.75	1.0	528	4.5
Mix 10	7.0	0.75	1.0	540	5.4
Mix 10	7.0	0.75	1.0	460	3.7
Mix 14	5.0	0.75	1.0	448.8	2.9
Mix 14	5.0	0.75	1.0	520.7	5.9
Mix 14	5.0	0.75	1.0	550.6	6.5
Mix 19	4.0	0.75	1.0	443.3	3.6
Mix 19	4.0	0.75	1.0	528.8	7.1
Mix 19	4.0	0.75	1.0	401.3	2.9

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

slow strength development up to 3 days (with a compressive strength of ${\sim}1$ MPa), 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 [17,61].

The higher dosage of 7% CaSO₄ in G (Mix 10) lead to an increased reaction of C₃A and C₄AF, which incorporated glucose and reduced the retardation of other cement components, having a higher strength performance than the mixture with 5% CaSO₄ (Mix 3). The use of 4% CaSO₄ 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% CaSO₄ in the presence of glucose (Mix 3 and Mix 6) and *W* having 5% and 4% CaSO₄ in the presence of glucose (Mix 16 and Mix 19), as presented in Fig. 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 CaSO₄ 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.

The produced WWCC 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 4. It can be seen that all produced boards showed higher or similar strength compared to the commercial WWCC (termed C_WWCC), indicating the validity of the binder composition proposed in this research.

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 C₃A 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 2.1. Although the heat release presented in Fig. 10d shows positive effects with *W* having 2.5% CaSO₄ (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 Fig. 10d. This caused a lack of interconnection between the wood-wool and a lower interaction with the soluble extractives from the wood-wool.

4. Conclusions

In this article, the hydration kinetics of cements is studied, and the retardation of sugars on two different cements with varying CaSO₄ 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 C₄AF, the compressive strength of mortars made with white cement is much greater.
- The dosage of CaSO₄ plays a very sensitive role on the hydration of cement containing glucose. For grey Portland cement, a slight reduction of CaSO₄ content to 4% already causes a flash set and a dramatic retardation. However, an increase of the CaSO₄ content to 7% leads to an increased heat release and compressive strength. For Portland white cement, the reduction of CaSO₄ 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 CaSO₄ content.

- Mortars and wood-wool cement composites using white cement with a reduced CaSO₄ content (4%) and using grey cement with an increased CaSO₄ 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.

Acknowledgments

The authors would like to acknowledge STW-foundation, Knauf Insulation, ENCI B.V., Eltomation, van Gansewinkel minerals for their financial support and provision of materials. Furthermore, special thanks to Q. Alam and V. Caprai for the valuable discussion and T. Druenen for helping with the experiments. Furthermore, the authors wish to express their gratitude to the following sponsors of the Building Materials research group at TU Eindhoven: Rijkswaterstaat Grote Projecten en Onderhoud; Graniet-Import Benelux; Kijlstra Betonmortel; Struyk Verwo; Attero; Rijkswaterstaat Zee en Delta-District Noord; BTE; V.d. Bosch Beton; Selor; GMB; Icopal; BN International; Knauf Gips; Hess AAC Systems; Kronos; Joma; CRH Europe Sustainable Concrete Centre; Cement & Beton Centrum; Heros; Inashco; Keim and Sirius International (in chronological order of joining).

References

- L.K. Aggarwal, J. Singh, Effect of plant fibre extractives on properties of cement, Cement Concr. Compos. 12 (1990) 103–108, http://dx.doi.org/10.1016/0958-9465(90)90047-2.
- [2] L.K. Aggarwal, S.P. Agrawal, P.C. Thapliyal, S.R. Karade, Cement-bonded composite boards with arhar stalks, Cement Concr. Compos. 30 (2008) 44– 51. http://linkinghub.elsevier.com/retrieve/pii/S0958946507001230 (accessed December 17, 2012).
- [3] P. Tang, M.V.A. Florea, P. Spiesz, H.J.H. Brouwers, Characteristics and application potential of municipal solid waste incineration (MSWI) bottom ashes from two waste-to-energy plants, Constr. Build. Mater. 83 (2015) 77–94, http://dx.doi.org/10.1016/j.conbuildmat.2015.02.033.
- [4] G.C.H. Doudart de la Grée, M.V.A. Florea, A. Keulen, H.J.H. Brouwers, Contaminated biomass fly ashes – characterization and treatment optimization for reuse as building materials, Waste Manage. (2015).
- [5] C.B. Cheah, M. Ramli, The implementation of wood waste ash as a partial cement replacement material in the production of structural grade concrete and mortar: an overview, Resour. Conserv. Recycl. 55 (2011) 669–685, http:// dx.doi.org/10.1016/j.resconrec.2011.02.002.
- [6] A.E. Abalaka, Effects of Sugar on Physical Properties of Ordinary Portland Cement Paste and Concrete, AU J.T. 14 (2011) 225–228.
- [7] H.F.W. Taylor, Cement chemistry, 1990.
- [8] V.S. Ramachandran, M.S. Lowery, Conduction calorimetric investigation of the effect of retarders on the hydration of Portland cement, Thermochim. Acta 195 (1992) 373–387, http://dx.doi.org/10.1016/0040-6031(92)80081-7.
- [9] A. Neville, Properties of concrete Fourth and Final Edition, 2002.
- [10] P.C. Hewlett, Lea's Chemistry of Cement and Concrete, 2004.
- [11] H. Huang, X.D. Shen, Interaction effect of triisopropanolamine and glucose on the hydration of Portland cement, Constr. Build. Mater. 65 (2014) 360–366, http://dx.doi.org/10.1016/j.conbuildmat.2014.04.077.
- [12] J. Cheung, A. Jeknavorian, L. Roberts, D. Silva, Impact of admixtures on the hydration kinetics of Portland cement, Cem. Concr. Res. 41 (2011) 1289–1309, http://dx.doi.org/10.1016/j.cemconres.2011.03.005.
- [13] A.W.C. Lee, Physical and mechanical properties of cement bonded southern pine excelsior board, Forest Prod. J. 34 (1984) 30–34.
- [14] A.W.C. Lee, P.H. Short, Pretreating hardwood for cement-bonded excelsion board.pdf, Forest Prod. J. 39 (1989) 68–70.
- [15] J. Mencnarowski, Personal communication Knauf insulation, (2014).
- [16] J.F. Young, A review of the mechanisms of set-retardation in portland cement pastes containing organic admixtures, Cem. Concr. Res. 2 (1972) 415–433, http://dx.doi.org/10.1016/0008-8846(72)90057-9.
- [17] W. Lieber, W. Richartz, Einfluss von Träthanolamin, Zucker and Borsäure auf das Erstarren und Erhärten von Zementen, Zement-Kalk-Gips 24 (1972).

- [18] Y. Yamamoto, Retarders for Concrete and Their Effects on Setting Time and Shrinkage: Interim Report (1972), http://dx.doi.org/10.5703/1288284313840. This.
- [19] N.B. Singh, Influence of calcium gluconate with calcium chloride or glucose on the hydration of cements, Cem. Concr. Res. 5 (1975) 545–550, http://dx.doi. org/10.1017/CB09781107415324.004.
- [20] N.B. Milestone, The effect of glucose and some glucose oxidation products on the hydration of tricalcium aluminate, Cem. Concr. Res. 7 (1977) 45–52.
- [21] N.L. Thomas, J.D. Birchall, The retarding action of sugars on cement hydration, Cem. Concr. Res. 13 (1983) 830–842.
- [22] M. Collepardi, S. Monosi, G. Moriconi, M. Pauri, Influence of gluconate, lignosulfonate or glucose on the C3A hydration in the presence of gypsum with or without lime, Cem. Concr. Res. (1984) 105–112.
- [23] B.Y. Yang, R. Montgomery, Alkaline degradation of glucose: effect of initial concentration of reactants, Carbohydr. Res. 280 (1996) 27–45, http://dx.doi. org/10.1016/0008-6215(95)00294-4.
- [24] V.S. Ramachandran, Concrete Admixtures Handbook, Concrete Admixtures Handbook. (1996) 410–517. doi:10.1016/B978-081551373-5.50011-8.
- [25] M. Bishop, A.R. Barron, Cement hydration inhibition with sucrose, tartaric acid, and lignosulfonate: Analytical and spectroscopic study, Ind. Eng. Chem. Res. 45 (2006) 7042–7049, http://dx.doi.org/10.1021/ie060806t.
- [26] P.A. Shaffer, T.E. Friedemann, Sugar Activation by Alkali., (1929).
- [27] J.U. Nef, Dissoziationsvorgange in der Zuckergruppe; Justus Liebigs Annalen Der Chemie. (1913).
- [28] J.H. Taplin, Discussion of "some chemical additions and admixtures in cement paste and concrete", 4th International Symposium on the Chemistry of Cement. (1962).
- [29] S. Suzuki, S. Nishi, The effects of saccharides and other organic compounds on the hydration of cement, Semento Gijutsu Nempo 13 (1959) 160–170.
- [30] P. Sandberg, C. Porteneuve, F. Serafin, J. Boomer, N. LoConte, V. Gupta, B. Dragovic, F. Doncaster, L. Alioto, T. Vogt, Effect of admixture on cement hydration kinetics by synchrotron XRD and isothermal calorimetry, in: Proceedings of the 12th International Congress on the Chemistry of Cement, 2007.
- [31] J.-P. Perez, D. Sorrentino, Influence of aluminate hydrate and iron hydroxide precipitation on early-age C3S hydration kinetics, in: Proceedings of the 12th International Congress on Teh Chemistry of Cement, 2007.
- [32] P. van Elten, Personal communication Eltomation, (2015).
- [33] H.W. Reinhardt, Beton als constructiemateriaal eigenschappen en duurzaamheid, Delft, 1998.
- [34] F.C. Jorge, C. Pereira, J.M.F. Ferreira, Wood-cement composites: a review, Holz Als Roh-Und Werkstoff 62 (2004) 370–377, http://dx.doi.org/10.1007/s00107-004-0501-2.
- [35] M.H. Simatupang, R.L. Geimer, Inorganic binder for wood composites: feasibility and limitations, in: Wood Adhesives, 1990, pp. 169–176. Madison, Wisconsin, USA.
- [36] A. Crumbie, G. Walenta, T. Füllmann, Where is the iron? Clinker microanalysis with XRD Rietveld, optical microscopy/point counting, Bogue and SEM-EDS techniques, Cem. Concr. Res. 36 (2006) 1542–1547, http://dx.doi.org/10.1016/ j.cemconres.2006.05.031.
- [37] N. Shanahan, A. Zayed, Cement composition and sulfate attack. Part I, Cem. Concr. Res. 37 (2007) 618–623, http://dx.doi.org/10.1016/j. cemconres.2006.12.004.
- [38] G.C.H. Doudart de la Gree, Q.L. Yu, H.J.H. Brouwers, Wood-wool cement board: optimized inorganic coating, in: Proceedings of the 14th International Inorganic-Bonded Fiber Composites Conference (IIBCC), 15–19 September 2014, Da Nang, Vietnam, 2014, pp. 154–164.
- [39] Tappi Method T 222 om-88, Acid-insoluble lignin in wood and pulp, Atlanta, GA, 1988.

- [40] Tappi Method UM 250, Acid-soluble lignin in wood and pulp, Atlanta, GA, 1985.
- [41] Tappi T264 om-88, Preparation of wood for chemical analysis, Atlanta, GA, 1996.
- [42] M.G. Tjoelker, A. Boratynski, W. Bugala, Biology and Ecology of Norway Spruce, 2007.
- [43] F. Bertaud, B. Holmbom, Chemical composition of earlywood and latewood in Norway spruce heartwood, sapwood and transition zone wood, Wood Sci. Technol. 38 (2004) 245–256, http://dx.doi.org/10.1007/s00226-004-0241-9.
- [44] Z. Shui, D. Xuan, H. Wan, B. Cao, Rehydration reactivity of recycled mortar from concrete waste experienced to thermal treatment, Constr. Build. Mater. 22 (2008) 1723–1729, http://dx.doi.org/10.1016/j.conbuildmat.2007.05.012.
- [45] C. Alonso, L. Fernandez, Dehydration and rehydration processes of cement paste exposed to high temperature environments, J. Mater. Sci. 39 (2004) 3015–3024, http://dx.doi.org/10.1023/B:JMSC.0000025827.65956.18.
- [46] Q. Zhang, G. Ye, Dehydration kinetics of Portland cement paste at high temperature, J. Therm. Anal. Calorim. 110 (2012) 153–158, http://dx.doi.org/ 10.1007/s10973-012-2303-9.
- [47] G.A. Khoury, C.E. Majorana, F. Pesavento, B.A. Schrefler, Modelling of heated concrete, Mag. Concr. Res. 77–101 (2002).
- [48] E.C. Standardization, EN 196-1, Methods of Testing Cement Part 1: Determination of Strength, (2005).
- [49] E.C. Standardization, EN 12089: Thermal insulating products for building applications - Determination of bending behavior, (1997).
- [50] S. Pourchet, L. Regnaud, J.P. Perez, A. Nonat, Early C3A hydration in the presence of different kinds of calcium sulfate, Cem. Concr. Res. 39 (2009) 989– 996, http://dx.doi.org/10.1016/j.cemconres.2009.07.019.
- [51] H. Minard, S. Garrault, L. Regnaud, A. Nonat, Mechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsum, Cem. Concr. Res. 37 (2007) 1418–1426, http://dx.doi.org/10.1016/j. cemconres.2007.06.001.
- [52] A. Cuesta, I. Santacruz, S.G. Sanfélix, F. Fauth, M.A.G. Aranda, A.G. De La Torre, Hydration of C4AF in the presence of other phases: a synchrotron X-ray powder diffraction study, Constr. Build. Mater. 101 (2015) 818–827, http://dx. doi.org/10.1016/j.conbuildmat.2015.10.114.
- [53] A. Quennoz, K.L. Scrivener, Hydration of C3A–gypsum systems, Cem. Concr. Res. 42 (2012) 1032–1041, http://dx.doi.org/10.1016/j. cemconres.2012.04.005.
- [54] S. Chatterji, J.W. Jeffery, Studies of early stages of paste hydration of cement compounds, J. Am. Cer. Soc. 45 (1962) 536–543, http://dx.doi.org/10.1111/ j.1151-2916.1962.tb11053.x.
- [55] M. Fukuhara, S. Goto, K. Asaga, M. Daimon, R. Kondo, Mechanisms and kinetics of C4AF hydration with gypsum, Cem. Concr. Res. 11 (1981) 407–414, http:// dx.doi.org/10.1016/0008-8846(81)90112-5.
- [56] FIB The International Federation for Structural Concrete, Corrosion protection of reinforcing steels, 2009.
- [57] A.M. Neville, Properties of concrete, Fourth and 2002.
- [58] W. Dosch, Interlamellar reactions of tetracalcium aluminate hydrates with water and organic compounds, Fifteenth Conference on Clays and Clay Minerals. (1967).
- [59] J.F. Young, Effect of organic compounds on the interconversions of calcium aluminate hydrates. Hydration of monocalcium aluminate, Am. Cer. Soc. 53 (1970) 65–69, http://dx.doi.org/10.1016/0008-8846(71)90088-3.
- [60] M. Horgnies, J.J. Chen, C. Bouillon, Overview about the use of Fourier Transform Infrared spectroscopy to study cementitious materials. Materials Characterisation VI, Comput. Methods Exp. 77 (2013) 251, http://dx.doi.org/ 10.2495/MC130221.
- [61] M.C. Garci Juenger, H.M. Jennings, New insights into the effects of sugar on the hydration and microstructure of cement pastes, Cem. Concr. Res. 32 (2002) 393–399, http://dx.doi.org/10.1016/S0008-8846(01)00689-5.