Cement recycling with help of biobased additives.

Report D2.2a Performance of ultrafine CDW as binder component: effect of the first generation biobased additives

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Report D2.2a
Performance of ultrafine CDW as binder component

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Contents

1 Introduction

1.1 Background of the research

The current most used material worldwide is concrete. Cement, one of the components of concrete, is responsible for about 7% of total CO_2 emissions in the planet. Half of this emissions is due to cement production. Therefore, alternative binders that can replace cement are of great contribution to reduce the environmental impact of concrete. At the same time, many concrete structures are reaching the end of their service life: they must be dismantled and in most cases demolished. The deposal of the demolished structures has become an issue since the concrete construction and demolition waste (CDW) must be disposed properly. An alternative that can help with the replacement of cement and the deposal of demolished concrete structures at the same time is recycling of the old cement paste. This is in line with the goals of the Dutch government which has as an aim by 2030 to reduce by 50% the CO_2 emissions of the construction industry.
In order to recycle the old cement paste to be used as new binder, this material must be finely grounded and then (preferably) reactivated. The current project focuses on the reactivation of the ground old cement paste by using biobased additives to enhance dissolution and precipitation.

1.2 Aim of this research

In this project, 2 streams of CDW are used. The source of the first is mixed concrete from different sources, referred to as CDW_MX and the second crushed railway sleepers, labelled as CDW_SLP. In previous work [1], a full characterization of these two waste streams was performed. In the current research, the two waste streams were used in combination with ground granulated blast furnace slag (GGBS), and inorganic additives as activators and set regulators to test their potential as binder to replace cement. In addition, a first assessment has been made of the performance of the first generation of biobased polymers developed by the WUR.
The first part of the research focuses on the potential of the CDW_MX as binder with Na_2SO_4 as set regulator and various amounts of GGBS as well as several types of biopolymers. The performance of the CDW_MX was determined as follows:

- The effect on the hardening of binder paste mixes with CDW_MX in combination with different contents of Na_2SO_4 and GGBS was investigated by means of the Vicat apparatus.
- Based on the results of the Vicat apparatus, a set of paste blends using CDW_MX, GGBS and Na_2SO_4 were tested by microcalorimetry to observe the impact of the different components on the heat flow and heat development. Some of these mixes were defined as benchmark on account of their performance.
- A second run of microcalorimetry tests was executed using the benchmark mixes in combination with different types and contents of biopolymers. To assess the effect of the biopolymers, the results obtained in terms of heat flow and heat development were compared with the ones of the benchmark mixes.
- Mechanical tests on mortar bars at different ages were performed on selected blends that showed promising results in the Vicat and microcalorimetry tests.

In the second part of the research, the CDW_SLP has been tested with a large range of inorganic additives as binder paste without using GGBS. It was considered that due to the homogeneity of these ultrafines and the pure Portland cement concrete that was used for its manufacturing, a high Ca-CSH cement was likely to be formed which on its own might have sufficient binding capacity. The hardening of pastes with large range of inorganic additives was investigated by means of the Vicat apparatus. Microcalorimetry experiments on these binder pastes have not been performed as it was supposed that the interpretation of the results of the first series was less straight forward, as will be discussed later on. Only CDW_SLP mortar bars without any inorganic additives have been tested as reference. Based on the hardening tests results, other mortar bars were tested with Na_2SO_4 as it was one of the best and most stable performing set regulators. It also serves as a starting point for further research with 20 % GGBS addition, similarly as for CDW_MX.

1.3 Content of this report

Chapter 2 provides an overview of the materials and the mix designs for the binder paste (Vicat and microcalorimetry) and the mortar (mechanical tests). Chapter 3 explains the experimental procedure for the Vicat hardening test, calorimetry test and mechanical tests. Chapter 4 and chapter 5 show the results of the experiments for CDW_MX and CDW_SLP, respectively. Chapter 6 discusses and analyses the results obtained and finally chapter 7 gives the conclusions of this report.

2 Experimental program

2.1 Materials

The following materials have been used in this study:

- Precursors:
  - Concrete construction and Demolition Waste Mixed (CDW_MX) provided by Urban Mine.
  - Concrete construction and Demolition Waste from sleepers (CDW_SLP) provided by Urban Mine.
  - ECO2CEM ground granulated blast-furnace slag (GGBS) supplied by Ecocem Benelux.
- Additives:
  - Sodium sulphate (Na_2SO_4) provided by Sigma Aldrich.
  - Anhydrate Calcium sulphate ($CaSO_4$) provided by Sigma Aldrich.
  - Sodium hydroxide (NaOH) provided by Sigma Aldrich.
  - Biopolymers provided by Wageningen University and Research (WUR). Details are given in table 2.1..

Table 2.1: Specification of the biopolymers used DS = degree of substitution, DO = degree of oxidation, Mw = Molecular weight, NM = not measured

TNO code MP2017-	WUR code	Modification/treatment	DS/DO	Mw (Dalton)
H2	IH227 Novicoll df	Original starch, Deep freezed	-	-
H6	ND IH254 C6	carbomethylation	0.12	4700
H7	ND IH255 C6	carbomethylation	0.35	NM
H9	ND IH266 OX	oxidation	0.16	NM
H10	ND IH280 OX	oxidation	0.22	7300
H11	NG IH281 OX	oxidation	0.16	NM

A description of the biopolymers is given in [2]. In brief, a starch product, Novidexx WD, has been modified in order to introduce a carboxylic group (−COOH). Three different types of modifications have been made: two oxidation modifications and one carbomethylation modification. The effect of the carbomethylation is the replacement of hydrogen by carbomethyl groups in some of the OH-functional groups, as shown in the figure below. The degree of substitution of hydrogen by a carbomethyl group after carbomethylation in H7 in higher than for H6 (DS = 0.35 versus 0.12).

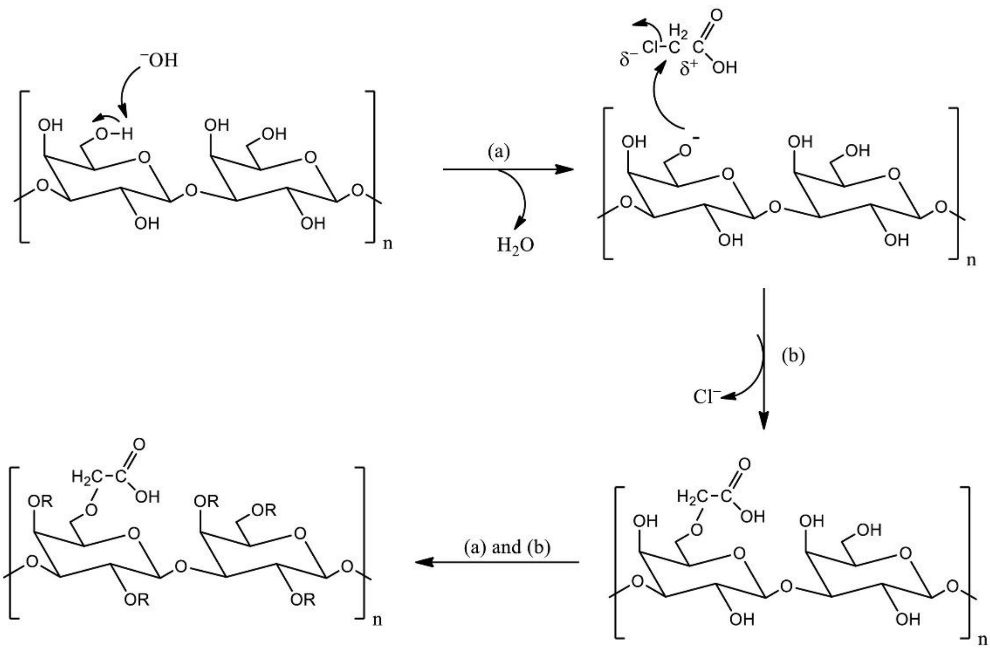


Figure 2.1 Sketch of the carbomethylation process (figure from [3]).

The effect of the oxidation process is that some hydroxyl groups are first oxidized to carbonyl groups and subsequently to carboxyl groups. The contents of the carbonyl and carboxyl groups in a starch molecule together define the degree of oxidation (DO). One such an oxidation process is shown in Figure 2.2. The degree of oxidation of H9 and H11 is 0.16, while that of H10 is 0.22. According to the information of the WUR, H9 and H11 were produced differently. No further information is however available.

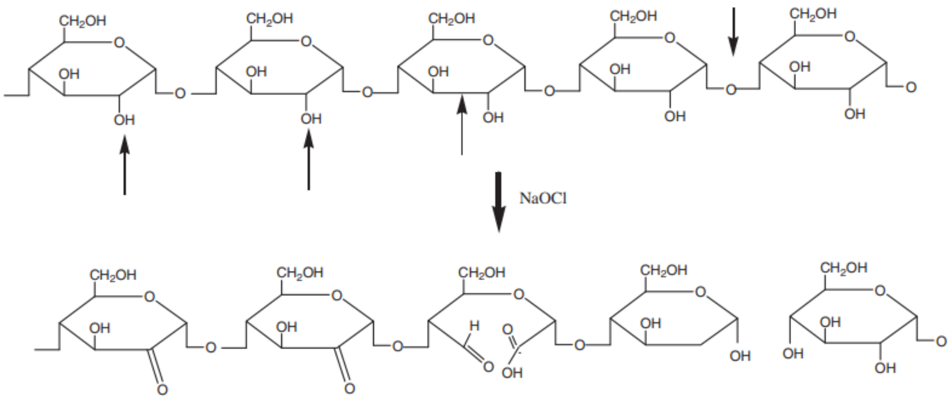


Figure 2.2 Sketch of the oxidation process (figure from[4]).

A description of the CDW streams is given in [1]. In brief, two different ultrafine powders from recycled concrete have been used, one from mixed types of concretes, labelled CDW_MX, and one from railway sleepers made from CEM I, labelled CDW_SLP. Some specifications of the CDW streams are given in Table 2.2, together with the used slag.

Table 2.2: Specification of the CDW ultrafines and slag used

	Solid density (kg/m^3)	D50 (μm)	Surface area (m^2/g)	In demi-water: pH (-)	Conductivity (S/m)	Zetapotential (mV)
CDW_MX	2320	20.1	15.2 (1.5)	12.6	0.35	0.6
CDW_SLP	2410	51.2	3.4	12.9	0.53	1.7
GGBS	2600	11.6	1.4	9.9	0.02	1.4

XRD analysis [2] showed that both streams consisted of quartz, calcium carbonate, albite and ettringite as crystalline phases, with portlandite in addition being present in the CDW_SLP. The quartz and albite are likely from milled sand and gravel, while the calcium carbonate may come from either carbonated cement products (portlandite or CSH) or aggregates or fillers. Ettringite is most likely a cement hydrate product. Most of the cement hydrates, however, will be amorphous. Furthermore, it can be deducted from the presence of the portlandite that not all cement paste of the sleepers (CDW_SLP) was carbonated.

XRF analysis of CDW_MX, combined with the composition of the most commonly used cements in the Netherlands, indicate that the CDW_MX contain possibly only 50 % old cement paste and 50 % milled sand and gravel, assuming all Ca is due to the cement and not due to carbonate-bearing aggregates or fillers and that blended cements have been used. No XRF-analysis of the sleeper ultrafines (CDW_SLP) is available.
Both ultrafines are basic: when mixed with water they both lead to a solution that has a pH of 12.6 (mixed concrete ultrafines) and 12.9 (sleeper ultrafines), indicative of an equilibrium with the calcium phases ($Ca(OH)_2$ or calcium-poor CSH) and some alkali. This also leads to reasonably high conductivities (0.35 S/m and 0.53 S/m for the mixed concrete and sleeper ultrafines, respectively).

2.2 Binder paste mix design

The (new) binder mix design depends on the type of test to be performed: hardening test or calorimetry test (See sections 3.1 and 3.2, respectively) as well as the composition of the two CDW-materials. For the CDW_MX, it was expected that the material could form a CASH binding system. It was established that from its chemical composition 50% of the solid material was old cement. In addition, based on XRD results, calcium sources could come from the old CSH as well as calcium carbonate (either from the aggregates, carbonated $Ca(OH)_2$ and/or carbonated CSH). For the silica, sources might come most likely from the CSH and/or to a lower extend from the (reactive) aggregates. Since these components have a low reactivity, GGBS has been added to enhance their capacity to form the desired binder. Sodium sulfate is used as set regulator.

For the CDW_SLP, derived solely–from concrete made with CEM I cement and containing Portlandite phases as identified in the XRD analysis, it was expected to be more reactive than CDW_MX and could independently form a binder with sufficient strength without the use of GGBS. Since one of the ambitious of the project was to develop a binder with 100% CDW, hardening tests were conducted using a wider range of inorganic additives combined with CDW_SLP alone, anticipating that its chemical composition would be sufficient to generate new reaction products resembling CSH.

2.2.1 Mixes for Vicat test

For the CDW_MX mixtures, up to 30 wt-% of the ultrafines were replaced by GGBS. In addition, sodium sulfate was added up to 4 % of the total mass of the precursors. For the CDW_SLP mixtures, sodium sulfate and anhydrate calcium sulphate were chosen as set regulator. NaOH and biopolymers H6 and H10 were chosen as activators (Table 2.4). Combinations of the different components were also tested (Table 2.4).
The mixes tested for the hardening tests of both CDWs streams are shown in Table 2.3 and Table 2.4. Because of the difference in water demand of both CDWs, to obtained a similar consistency, the w/b ratio of the CDW-MX had to be higher than for the CDW_SLP.

Table 2.3: Mixes for the quick scan hardening tests for CDW_MX, with and without slag and Na_2SO_4 as wt-% on total binder.

Mix No.	**Mass percentage – w/b = 0.45**	
	Ratio by mass CDW_MX/GGBS	**Na_2SO_4 (wt.%)**
1 - 4	70/30, 80/20, 90/10 and 100/0	0.0
5 - 8	70/30, 80/20, 90/10 and 100/0	1.0
9 - 12	70/30, 80/20, 90/10 and 100/0	2.0
13 - 16	70/30, 80/20, 90/10 and 100/0	4.0

Table 2.4: Mixes for the quick scan hardening test for CDW_SLP ; additives as wt.% on CDW_SLP content (= total binder).

	Percentage of additives used by mass of CDW_SLP – w/b = 0.40				
Mix No.	**Na_2SO_4**	**$CaSO_4$**	**NaOH**	**H6**	**H10**
Reference					
17 – 19	1%, 2% and 4%				
20 – 22		1%, 2% and 4%			
23 – 25			1%, 2% and 4%		
26 – 28	1%, 2% and 4%		1%		
29 – 31		1%, 2% and 4%	1%		
32 – 34	1%, 2% and 4%		4%		
35 - 37		1%, 2% and 4%	4%		
38				0.25%	
39					0.25%
40	4%			0.25%	
41	4%				0.25%
42		4%		0.25%	
43		4%			0.25%
44			4%	0.25%	
45			4%		0.25%

In the mix design procedure, the mass of the Na_2SO_4 and the biopolymers are taken as a fixed percentage of total mass of CDW and GGBS.
Table 2.5 shows an example of a mix design of 80% CDW + 20% GGBS + 4% Na_2SO_4 and w/b = 0.45. The same mix design was used for the calorimetry mixes presented in the following section.

Table 2.5: Mix design example of paste, in wt.%.

CDW	53.0
GGBS	13.3
Total precursors	**66.3**
4 wt.% Na_2SO_4	2.65
Total solid components	**69.0**
Water	31.0 (w/b = 0.45)

2.2.2 Mixes for calorimetry test

An overview of the tested compositions for microcalorimetry is given in Table 2.6. Since in this test the mix is placed in a sample holder using a pipet, the mix had a more fluid consistency than the ones for the hardening test. Therefore a w/b of 0.65 was used instead of 0.45. The first two batches were with 100/0 and 80/20 blends of CDW_MX and GGBS and various amount of sodium sulphate as set regulator; to be used as benchmark to compare with the mixes with biopolymers. In the other batches different biopolymers with different concentrations were added to the mix 80% CDW_MX + 20% GGBS + 4% Na_2SO_4 from the benchmark.

Table 2.6: Mixes for calorimetry tests for CDW_MX; with and without slag and set regulator Na_2SO_4 and biopolymers as wt.% on total binder.

Batch	**Precursors (wt.% of precursors)**		**Na_2SO_4 (wt.% of precursor)**	**Biopolymer (wt.% of precursor)**	**w/b**	**No. of measurements**
	CDW_MX	**GGBS**				
1	100	0	0, 1%, 2% and 4%	-	0.65	4
2	80	20	0, 1.0%, 2% and 4%	-	0.65	4
3	80	20	4%	0.1%, 0.25%, 0.5% and 1.0% H2	0.65	4
4	80	20	4%	0.1%, 0.25%, 0.5% and 1.0% H6	0.65	4
5	80	20	4%	0.1%, 0.25%, 0.5% and 1.0% H7	0.65	4
6	80	20	4%	0.1%, 0.25%, 0.5% and 1.0% H9	0.65	4
7	80	20	4%	0.1%, 0.25%, 0.5% and 1.0% H10	0.65	4
8	80	20	4%	0.1%, 0.25%, 0.5% and 1.0% H11	0.65	4

2.3 Mortar mix design

2.3.1 Water demand

The water demand is defined as the mass of water needed for a powder to reach a paste with an earth dry consistency divided by the mass of the same powder. Figure 2.3 shows an example of the earth dry consistency for the CDW_MX. The earth dry consistency is defined as the point in which the paste has sufficient cohesion to form a ball without cracking when handling. The water demand is obtained without prior drying and thus includes the moisture content as received. Results are given in Table 2.7 for the solid materials.

Figure 2.3 Earth dry consistency for CDW_MX during water demand test

Table 2.7: Water demand of the ultrafines and slag.

	Water demand (g/g as received material)	**Moisture content (g / g dry material)**	**Total water demand (g/g dry material)**	**Surface area (m^2/g)**	**Water demand (g/m^2)**
CDW_MX	0.40	0.23	0.77	15.2	0.05
CDW_SLP	0.30	0.07	0.40	3.4	0.12
Slag	0.40	0.00	0.40	1.4	0.29

The results for the various mixtures are shown in Table 2.8.

Table 2.8: Water demand, blends with CDW_MX and CDW_SLP

<table>
<tr><th rowspan="2">Mix</th><th colspan="5">Mass (g)</th><th rowspan="2">w/b – Only water added</th><th rowspan="2">w/b – Including water from moisture content</th></tr>
<tr><th>CDW _MX</th><th>CDW _SLP</th><th>GGBS</th><th>Water added</th><th>Water from CDW moisture content</th></tr>
<tr><td>Benchmark: 80 CDW_MX + 20 GGBS</td><td rowspan="2">80</td><td></td><td rowspan="2">20</td><td>40</td><td>18.4</td><td>0.4</td><td>0.58</td></tr>
<tr><td>Benchmark + 0.25%H2</td><td></td><td>50</td><td>18.4</td><td>0.5</td><td>0.68</td></tr>
</table>

Mix	Mass (g)					w/b – Only water added	w/b – Including water from moisture content
	CDW _MX	CDW _SLP	GGBS	Water added	Water from CDW moisture content		
Benchmark + 0.25%H6				36	18.4	0.36	0.54
Benchmark + 0.25%H10				36	18.4	0.36	0.54
80 CDW_SLP+ 20 GGBS		80		33	5.6	0.34	0.40

2.3.2 Mix design

Based on the results of the calorimetry and the Vicat tests, 7 binder composition were defined for the mortar, 4 using CDW_MX and 3 using CDW_SLP. The mortar mixes were design with a similar earth dry consistency and with similar ratios between the paste and the aggregate content. Table 2.9 mortar to
Table **2.11** present the mass in kg per m^3 mortar, volume in m^3 per m^3 mortar and relevant data of the mixes respectively.

Table 2.9 Mortars mix design in kg / m^3 mortar.

	Mass per m^3 mortar (kg)								
	CDW_MX	CDW_SLP	GGBS	Na_2SO_4	Biopol.	Water binder	Sand - EN 196	Water / sand	Total
80 CDW_MX + 20 GGBS + 4% Na_2SO_4	300.2	-	75.0	15.0	0.00	153.1	1600.4	48.0	2191.7
80 CDW_MX + 20 GGBS + 4% Na_2SO_4 + 0.25% H2	264.1	-	66.0	13.2	0.83	172.0	1600.4	48.0	2164.5
80CDW_MX + 20GGBS + 4% Na2SO4 + 0.25%H6	311.6	-	77.9	15.6	/0.97	145.9	1600.4	48.0	2200.4
80CDW_MX + 20GGBS + 20GGBS 4% Na2SO4 + 0.25%H10	311.6	-	77.9	15.6	0.97	145.9	1600.4	48.0	2200.4
100CDW_SLP	-	422.1	-	-	-	162.1	1548.6	46.5	2179.3
100CDW_SLP + 2% Na2SO4	-	413.4	-	8.3	-	161.9	1550.3	46.5	2180.4
80CDW_SLP + 20GGBS	-	345.9	86.5	-	-	169.3	1536.1	46.1	2183.8

Table 2.10 Mortars mix design in m3 per m3 mortar.

	Volume per m^3 (m^3 mortar) – Theoretical air content = 2%								
	CDW_MX	CDW_SLP	GGBS	Na2SO4	Biopol.	Water binder	Sand - EN 196	Water / sand	Total
80 CDW_MX+ 4% Na_2SO_4	0.13	-	0.03	0.006	-	0.15	0.62	0.05	1.0
80 CDW_MX + 20 GGBS + 4% Na_2SO_4 + 0.25% H2	0.12	-	0.02	0.005	0.0008	0.17	0.62	0.05	1.0
80 CDW_MX + 20 GGBS + 4% Na_2SO_4 + 0.25% H6	0.14	-	0.03	0.006	0.0010	0.15	0.62	0.05	1.0
80 CDW_MX + 20 GGBS + 4% Na_2SO_4 + 0.25% H10	0.14	-	0.03	0.006	0.0010	0.15	0.62	0.05	1.0
100CDW_SLP	-	0.18	-		-	0.16	0.60	0.05	1.0
100 CDW_SLP + 2% Na_2SO_4	-	0.17	-	0.003	-	0.16	0.60	0.05	1.0
80 CDW_SLP + 20 GGBS	-	0.14	0.03		-	0.17	0.59	0.05	1.0

Table 2.11 Mortars mix design relevant properties (per kg mortar or m^3 mortar).

	Density (kg/ m^3)	Paste/Agg (kg/kg)	Paste/Agg (m^3/m^3)	w/b (kg/kg)	w/b (m^3/m^3)
80 CDW_MX + 20 GGBS + 4% Na_2SO_4	2192	0.34	0.55	0.40	0.93
80 CDW_MX + 20 GGBS + 4% Na_2SO_4 + 0.25% H2	2164	0.32	0.55	0.50	1.19
80 CDW_MX + 20 GGBS + 4% Na_2SO_4 + 0.25% H6	2200	0.34	0.55	0.36	0.85
80 CDW_MX + 20 GGBS + 4% Na_2SO_4 + 0.25% H10	2200	0.34	0.55	0.36	0.85
100 CDW_SLP	2179	0.38	0.60	0.38	0.92
100 CDW_SLP + 2% Na_2SO_4	2180	0.38	0.60	0.38	0.92
80 CDW_SLP + 20 GGBS	2184	0.39	0.61	0.39	0.97

3 Experimental procedure and test program

3.1 Quick scan hardening test for CDWs on binder paste

A quick scan hardening test for the two types of CDWs was performed using a Vicat apparatus to assess their potential hardening on its own or in combination with different additives (See section 2.2.1). Three fall heights of fine needle were chosen with respect to the surface of the samples: 0 mm, 10 mm and 30 mm. At a height of 0 mm, the needle was placed on the binder paste surface. For every height, the needle penetration was recorded.
By definition, the samples reach their final hardening when the needle penetration is 0-2 mm from a 30 mm height drop. This range is chosen because the quality of the surface is sometimes lower while the underlining paste is already quite strong. To prevent that this surface effect leads to wrong conclusions, a 2 mm penetration criteria has been set. If the needle penetration reaches a value that is the same as the thickness of the samples (12 mm for CDW_MX and 11 mm for CDW_SLP), the specimens have not reached sufficient hardening for the given needle drop height. All the samples had a diameter of 50 mm, as presented in Figure 3.1.

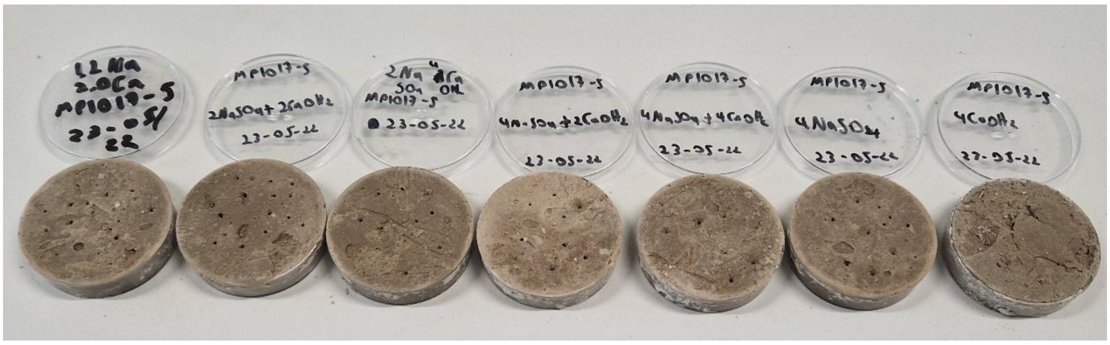


Figure 3.1 Quick hardening test samples.

During the test, the surface of the samples is kept wet, to prevent potential (false) hardening by drying. If this phenomenon takes place, the hardening of the samples would be overestimated. The samples were measured until the final hardening was obtained or until the moment in which the needle penetration remained constant in time and it was considered that the mix would not develop hardening properties any further.

3.2 Isothermal calorimetry test

3.2.1 Definition of terms used

The following definitions are used in this report:

- <u>Calorimetry:</u> Calorimetry is the method of determining the change in energy of a system by measuring its heat exchange with the surroundings under specific constrains, in this case under constant temperature.

- Heat flow: is the amount of heat that is transferred per unit of time in a material, usually measured in watt (joules per second)
- Normalized heat flow: The normalized heat flow is the value obtained after dividing the heat flow by the mass of the reactive material of the sample (See § 3.2.2). In the current document, only the normalized heat flow is presented.
- Heat: is the cumulative value of the heat flow. It is expresses in joules.
- Normalized heat: The normalize heat is the value obtained after dividing the heat by the mass of the reactive material of the sample (See 3.2.2). In the current document, only the normalized heat is presented.
- Sample: sample refers to the binder of interest whose heat development will be studied. In this case, it refers to the blends of GGBS and CDW.
- Reference: reference is the inert material that with the correct mass has the same heat capacity as the sample. In this case, quartz sand was used as reference.
- Channels: An 8 channel setup was chosen for the experiment. Each channel has two slots, one for the sample and the other for the reference. Figure 3.2 shows the setup used:

Figure 3.2 TAM Air setup with 8 channels.

3.2.2 TAM Air setup

For the setup of the TAM Air, the temperature was set at 25 °C and in the software the "Ampoule experiment" option was chosen. For the data collection, the signal and the raw data of the sample and the reference were recorded.
The TAM Air records the heat flow and heat of each sample. The measurements were normalized based on the mass of the solids of the samples. The mass of the water was not included since the chemical reaction and produced heat (between solid and water) is contributed to the solid (to prevent it to be counted twice). The samples had a water to binder ratio in mass (w/b) of 0.65. For a sample of 10 g, the samples were composed by 6.06 g of solid parts and 3.94 g of water. Thus, the heat flow and heat measured were normalized by 6.06 g.

3.2.3 Mass of reference material

The mass of the reference material is a function of its own specific heat, and the mass and specific heat of the components of the mix as shown in equation 3.1. Using as an input the mixes provided in section 2.2.2 and the specific heat of the components shown in Table 3.1, the mass of the reference material is obtained. Since all the samples have a mass of 10 g and a w/b = 0.65, the mass of the reference material was the same for all of them.

$$m_r = \frac{c_c m_c + c_w m_w}{c_r} \quad (3.1)$$

Where:
- m_r: Mass of the reference sample
- m_c: Mass of binding material
- m_w: Mass of water
- C_c: Specific heat of cement
- C_w: Specific heat of water
- C_r: Specific heat of reference sample

Table 3.1: Heat capacity of the used materials

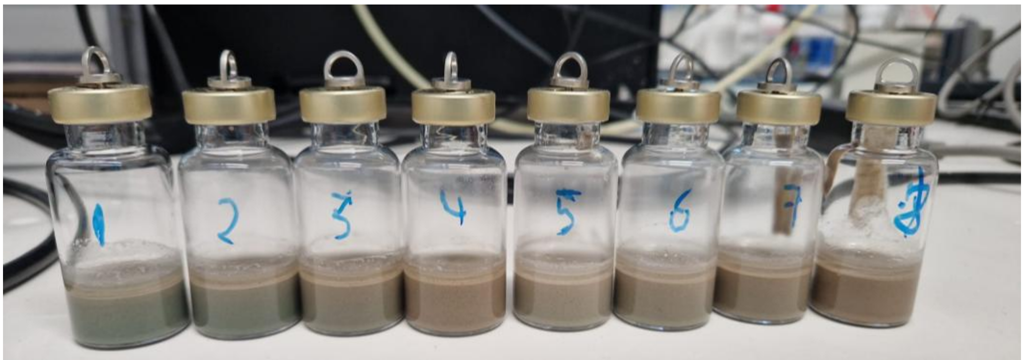
Material	Specific heat (J/gK)
Quartz (sand)	0.76
Binder	0.75
Free Water	4.2
Water in paste	3.2

3.2.4 Mixing procedure and calorimetry test

First, the reference material (quartz sand) was placed in each of the ampoules. Later, for the mixing procedure of the samples, the dry components of the mixes were mixed first in a container by means of shaking for 1 minute. Subsequently, water was added to the container and the mixing procedure was repeated for another minute. Afterwards, with a pipette, the slurry of the mixes was placed in the ampoules. Finally, each sample and a reference were placed one by one inside the TAM Air and the calorimetry test was set to run.

3.2.5 Hardening assessment

After the calorimetry measurements were finalized, the ampoules were broken and the samples were carefully extracted. Subsequently, a hardening test was made using the Vicat needle (fall height = 30mm) following the same procedure of section 3.1. Figure 3.3 shows an example of (a) the samples after the calorimetry test and (b) after the Vicat test.



(a)

(b)

Figure 3.3 (a) Samples after calorimetry samples. (b) Same samples after Vicat test.

3.3 Mortar bars

3.3.1 Mixing procedure

The mixing procedure used was the same for all the mixes. It is shown in Table 3.2.

Table 3.2 Mixing procedure

	Material to be added/action to be done	Speed mixer	Time (min)
1	Sand	1	0.5
2	Powders	1	1
4	Water (Water goes last)	1	1.5
5	Rest		1
6	Final mixing	2	1

After casting, the molds were wrapped and left in a controlled environment of 20 °C/65 %RH. After 24 hours, the samples were demolded, wrapped and stored again in a controlled environment of 20 °C/65 %RH until the day of testing.

3.3.2 Mechanical test

The mortar bars were tested in two-fold for three point bending and compressive strength. The tests were executed following the guidelines in the NEN-EN 196-1 [5]. Figure 3.4 shows the set-up used. The ages of the specimens at testing were 1, 7 and 34 days. When the samples did not harden at the age of testing, the strength was taken as zero and a new age for testing was defined.

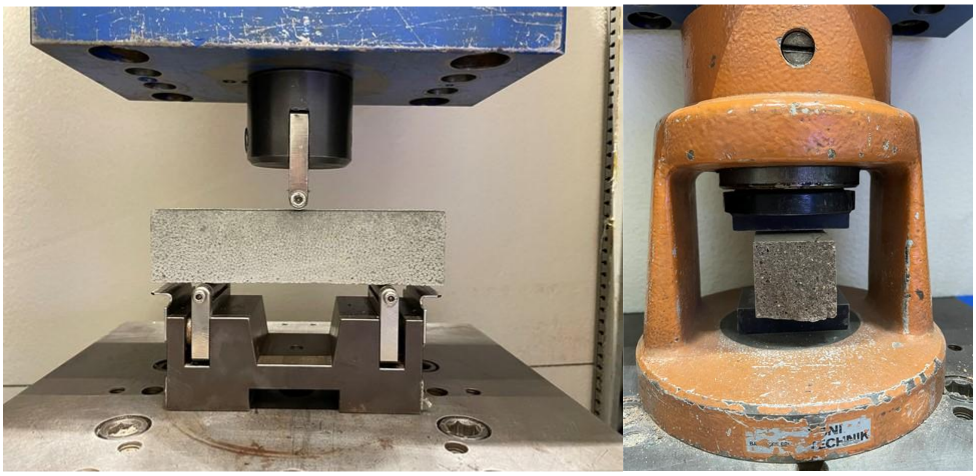


Figure 3.4 Experimental setup for 3-point bending strength and compressive strength.

4 Results for CDW_MX

4.1 Quick scan hardening test on paste

Figure 4.1 to Figure 4.4 present the results of the quick scan hardening test by means of the Vicat apparatus with various amounts of sodium sulphate as set regulator after 3 or 4 days of hardening. Figure 4.1 shows that blending CDW_MX with slag up to 70 % / 30 % does no lead to hardening of the pastes within 3 or 4 days. For all the samples without Na_2SO_4, the needle penetrates the samples completely, even at a fall height of 0 mm. Adding Na_2SO_4 to the CDW_MX without any slag also does not lead to hardening within the time of testing, with the exception of the 4 wt.% Na_2SO_4 addition at a fall height of 0 mm. In all cases, for the mixes with 1.0 wt.% or more Na_2SO_4, the replacement of only 10 wt.% CDW_MX by GGBS reduced the needle penetration considerably. By replacing 20 wt.% CDW_MX, the needle penetration reduced further but less compare to the initial replacement. Replacing 30 wt.% CDW_MX, the results were not further improving compared to the 20 wt.% CDW_MX replacement.

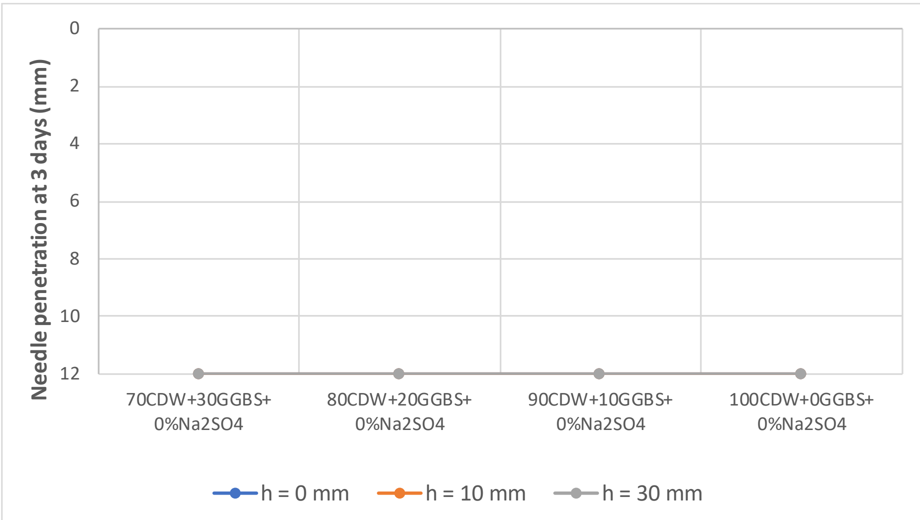


Figure 4.1 Needle penetration with variation in the CDW_MX/GGBS content without Na_2SO_4.

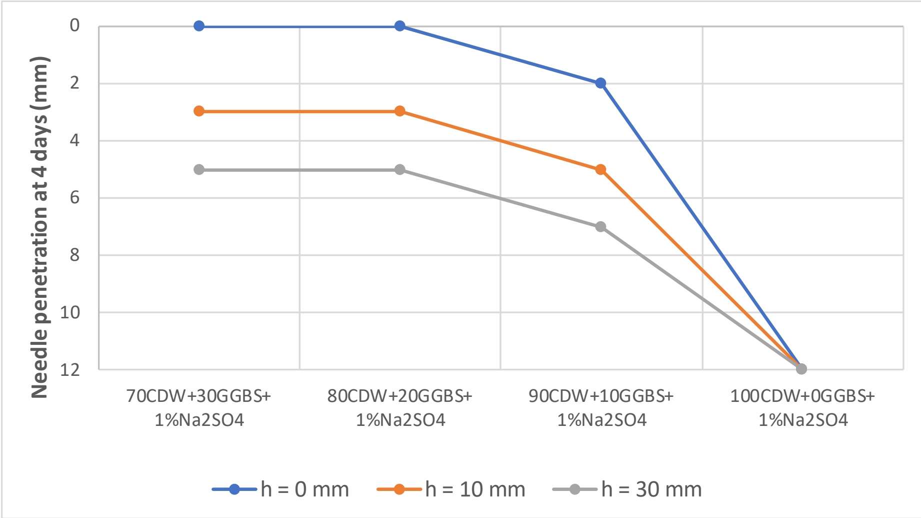


Figure 4.2 Needle penetration with variation in the samples CDW_MX/GGBS content with 1% Na_2SO_4.

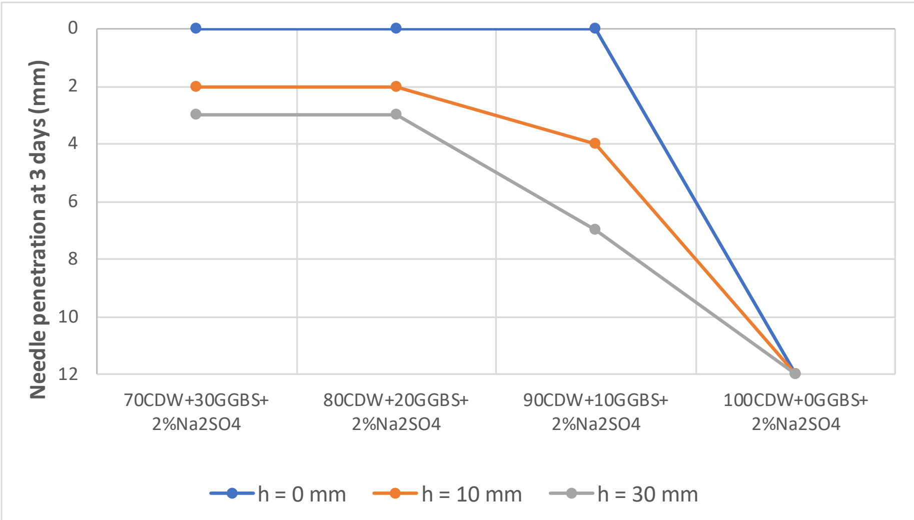


Figure 4.3 Needle penetration with variation in the samples CDW_MX/GGBS content with 2% Na_2SO_4.

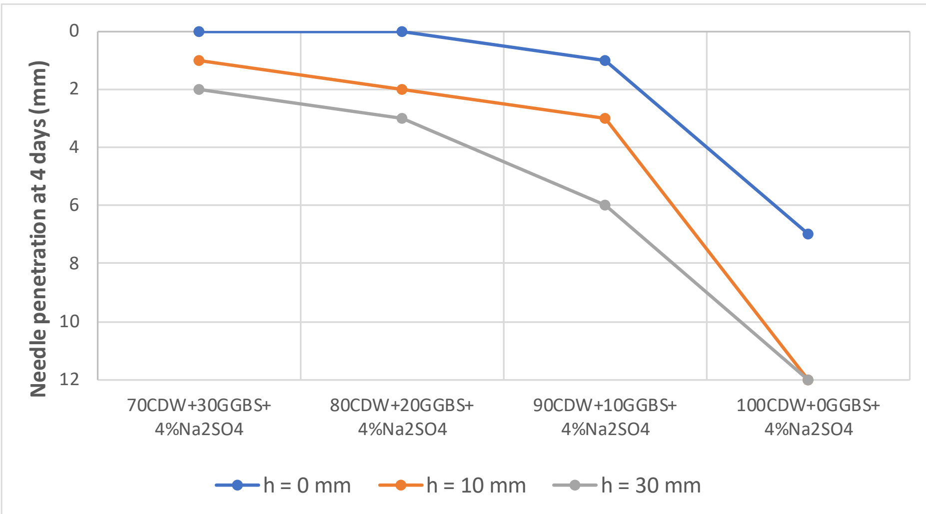


Figure 4.4 Needle penetration with variation in the samples CDW_MX/GGBS content with 4% Na_2SO_4.

Based on the results of the previous figures, Figure 4.5 presents a contour plot that relates the CDW_MX and Na_2SO_4 contents with the needle penetration at a height of 30 mm. The data used corresponds to the measurements at 3 days for the mixes with 0 and 2 % Na_2SO_4 and to the measurements at 4 days for the mixes with 1 % and 4 % Na_2SO_4, respectively. Although the age of testing is different, based on the microcalorimetry and mechanical strength results, it is warranted to assume that the one day difference does not have a major impact in the overall results. The graph shows that for a 100 % CDW_MX content, the amount of Na_2SO_4 does not have any impact on the needle penetration. Meanwhile, for CDW_MX contents between 70 and 90 %, an increase in the Na_2SO_4 content reduces the needle penetration, although the minimum penetration value still depends on the content of CDW_MX. The needle penetration reaches its lowest value when using CDW_MX contents between 70 and 80% and at least (based on the contour plot) 1.8 % Na_2SO_4. The needle penetration reduces with lower content of CDW_MX and with higher amounts of Na_2SO_4.

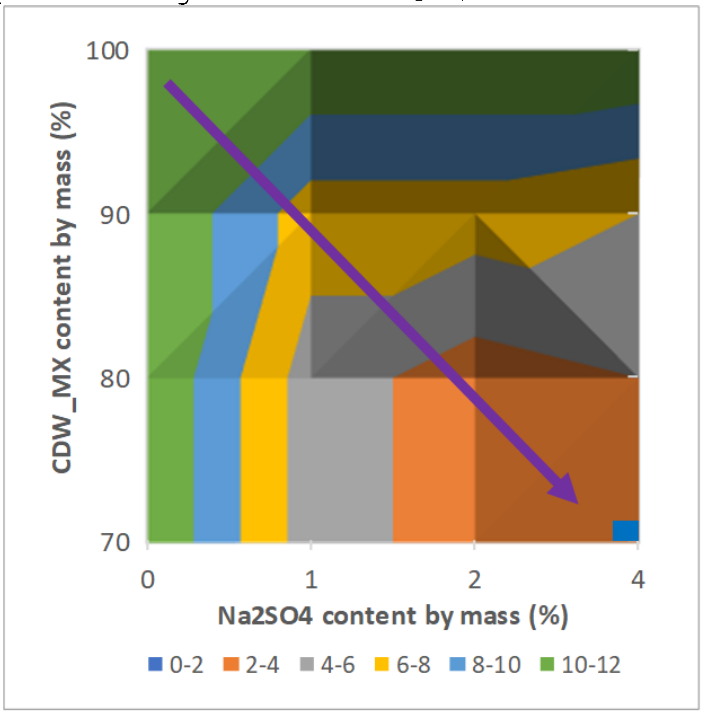


Figure 4.5 Contour plot, CDW_MX, relation between CDW_MX content, Na_2SO_4 content and needle penetration at (h = 30 mm) after 4 days for 1 % and 4 % Na_2SO_4 content and after 3 days for 0 % and 2 % Na_2SO_4 content. The purple arrow indicates the average effect of the slag + Na_2SO4 addition.

Based on these results, it was decided to choose 2 benchmark mixes for the calorimetry test. The first only the CDW with different Na_2SO_4 ratios and the second 80 CDW + 20 GBBS with different Na_2SO_4 ratios. The 80/20 ratio of CDW and GGBS was chosen over 70/30 in order to have a CDW-content as high as possible.

4.2 Isothermal calorimetry for binder paste with CDW_MX

4.2.1 Benchmark: Mixes with different ratios of CDW_MX, GGBS and Na_2SO_4

Figure 4.6 and Figure 4.7 present the normalized heat flow and cumulative normalized heat flow for the 100 % CDW_MX mixes with various amount of sodium sulfate as set regulator. In addition, for each mix the penetration depth (p), after the calorimetry measurements were finished, is indicated in Figure 4.7. It can be seen that although higher amounts of sodium sulfate result in higher heat production, none of the mixes has hardened within the time of testing (ca. 64 hours), as penetration depths have a maximum of 12 mm. This correlates well with the quickscan hardening test results shown in Figure 4.4.

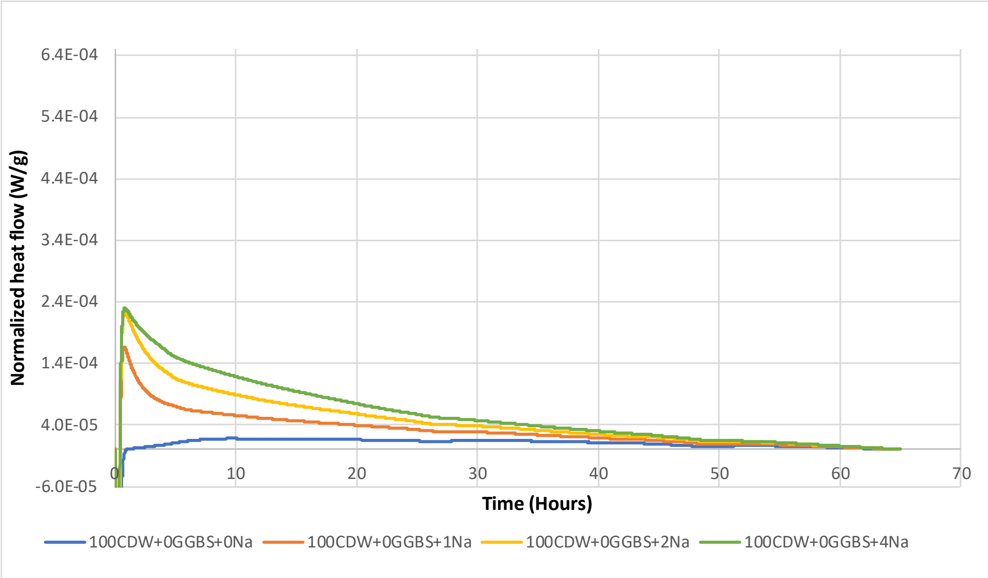


Figure 4.6 Normalized heat flow, samples with 100 CDW_MX + 0 GGBS and variation of Na_2SO_4 content.

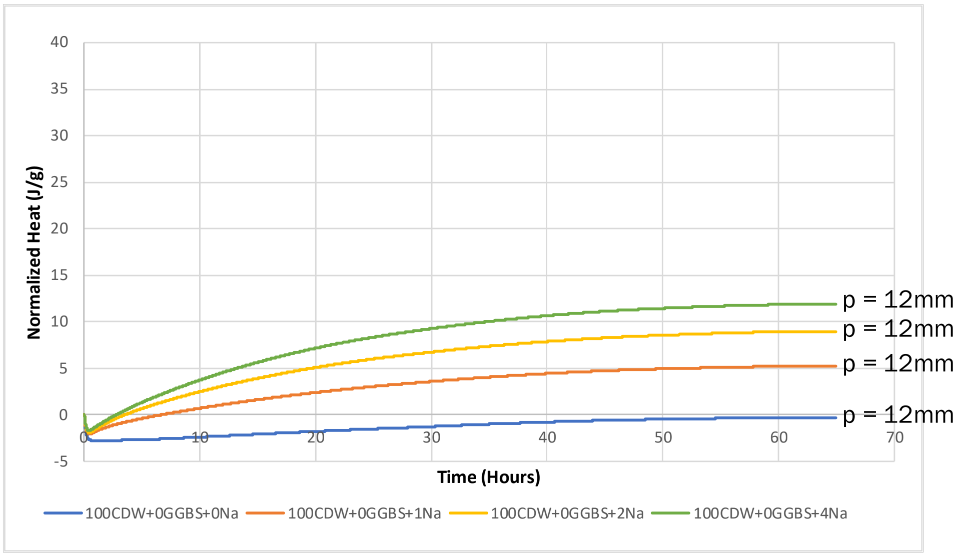


Figure 4.7 Normalized heat, samples with 100 CDW_MX + 0 GGBS and variation of Na_2SO_4 content with needle penetration (p) at a fall height of 30 mm.

Figure 4.8 and Figure 4.9 present the normalized heat flow and normalized heat as well as the penetration depth (p) after the measurements were finished for the blends of 80 % CDW_MX and 20 % slag with various amounts of Na_2SO_4. The increase in Na_2SO_4 concentration has two main effects on the heat development peak: it increases the peak value and slightly delays the time at which the peak occurs. Initially, as Na_2SO_4 concentration increases from 0% to 1%, the peak value increases considerably. However, as the concentration rises from 1% to 2%, the rate of increase is smaller, and reduces further from 2% to 4%. Similarly, the delay in the peak time follows this trend: it is larger from 0% to 1%, less from 1% to 2%, and even smaller from 2% to 4%. This pattern suggests that the effect of Na_2SO_4 decreases as larger amounts are added. It is likely that beyond a certain concentration, the peak value might reach a plateau, and further delays in the peak time may no longer occur.
The mixes that reach the highest heat flow peak values also reach the maximum heat and show lower needle penetration by the end of the measurements. However, none of the mixes can be considered fully hardened, as the penetration depth remains above 2 mm. Similar results were observed in the quick scan hardening test (see Figures 4.1 to 4.4).

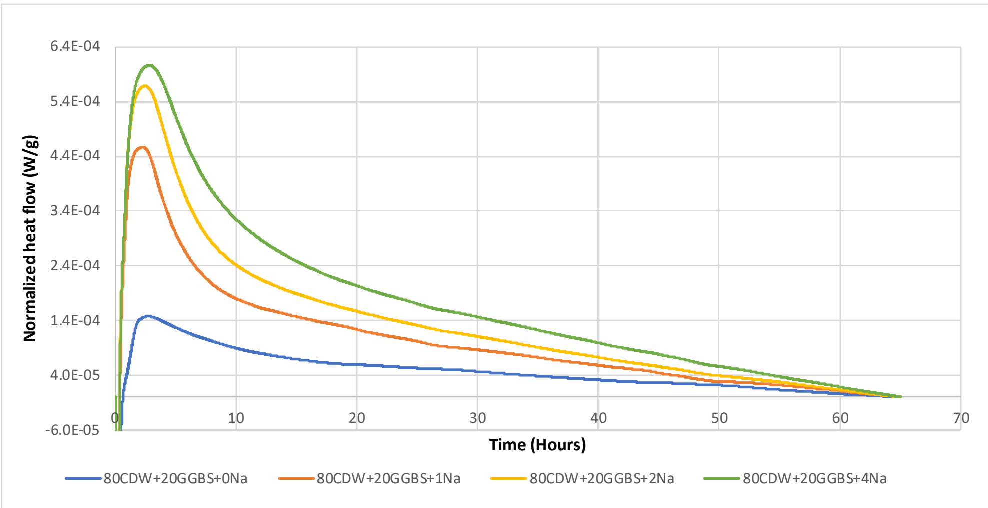


Figure 4.8 Normalized heat flow, samples with 80 CDW_MX +20 GGBS and variation of Na_2SO_4 content.

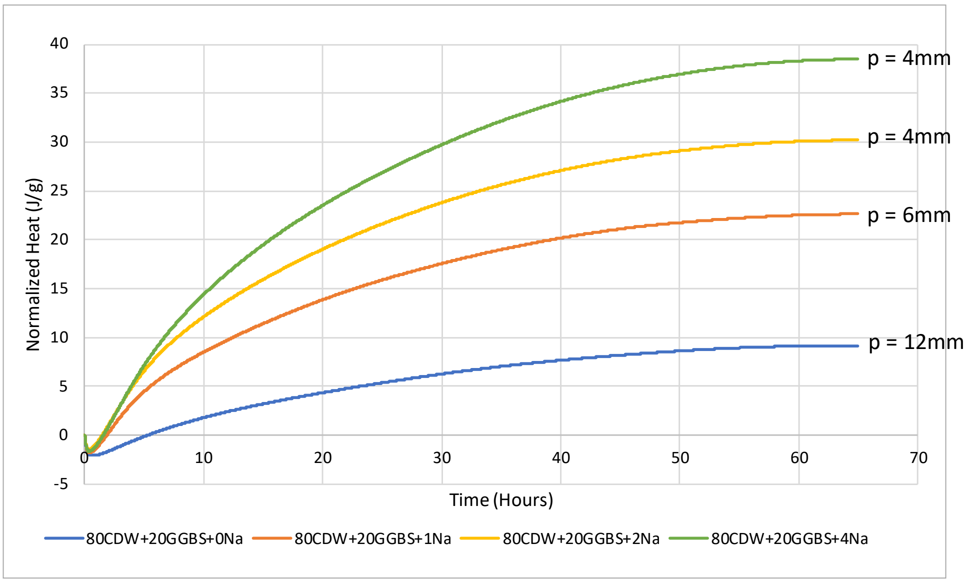


Figure 4.9 Normalized heat, samples with 80 CDW_MX + 20 GGBS and variation of Na_2SO_4 content with needle penetration (p) at a fall height of 30 mm.

The samples with the highest heat production have the lowest penetration depth, showing a direct relation between heat production and hardening. For the mixes presented in this section, it can also be observed that at the end of the test, the heat production has become zero, which possibly indicates that no further reactions (with heat production) are taking place. This possibly indicates that further hardening may be (very) slow or even absent. In the quick scan hardening test, the same results were found. Further discussion is given in section 6.1.

4.2.2 Mixes with 80 % CDW_MX, 20 % GGBS, 4 % Na_2SO_4 and different types and contents of biopolymers

For the mixes with biopolymer H2, Figure 4.10 presents the normalized heat flow and Figure 4.11 presents the normalized heat and the penetration depth (p) after the measurements were finished for a fall height of 30 mm.
It can be seen that the major effect of the biopolymer on the heat production is that the peak is decreasing, although the time at which this peak is reached is also slightly delayed. These effects increase with H2-dosage. At 0.1 wt.% (relative to precursors), the biopolymer H2 has little effect. Especially the heat production on the long term decreases to nearly zero, as can also be observed if no H2 is added. For the higher dosages, however, the heat production remains high. The highest continued heat production and total heat comes from the 0.25 wt.% H2-mix and declines again with higher dosages, indicating optimum behaviour.
In combination with the penetration depths, it can be concluded that the effect of the H2 as biopolymer is to delay and decrease the initial reaction rate, but at the right dosage can lead to prolonged heat production and longer ongoing reactions. The cumulative effect is tested only up to 64 hours but it seems that despite an almost 30 % higher heat production at that age for the 0.25 wt.% H2 dosage, the hardening is similar as for the mix without biopolymer. Higher H2 dosages with less additional heat development have also less favourable hardening. Apparently, there is an adverse effect of the biopolymer, hampering hardening to some extent.

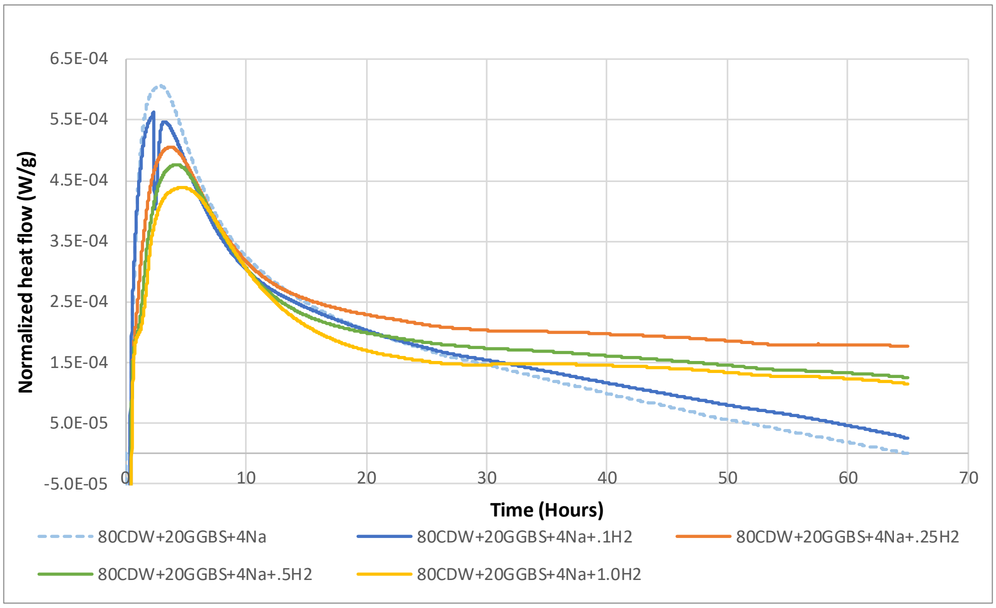


Figure 4.10 Normalized heat flow, samples with 80 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H2 content.

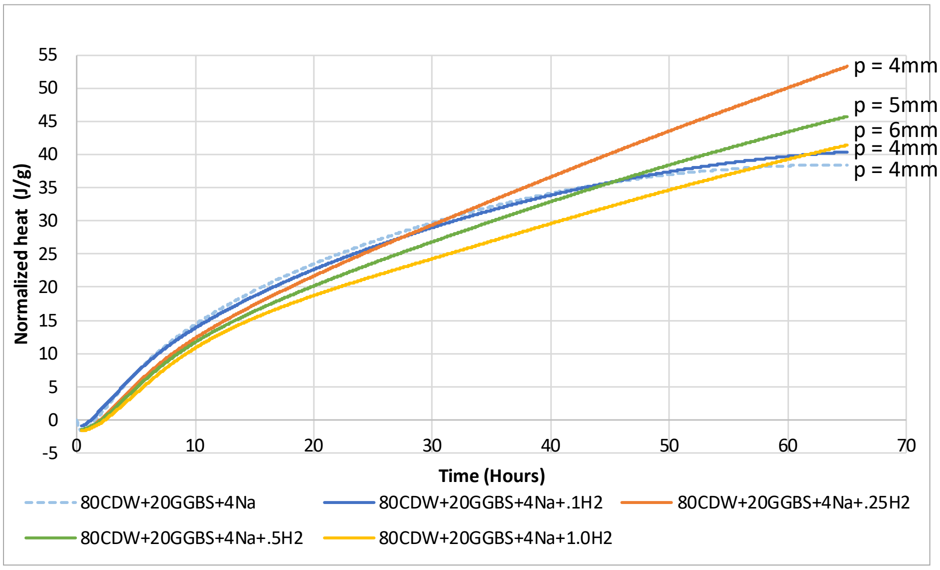


Figure 4.11 Normalized heat, samples with 80 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H2 content with needle penetration (p) at a fall height of 30 mm.

Like biopolymer H2, biopolymer H6 reduces the heat flow peak with increasing content (Figure 4.12 and Figure 4.13). The reduction for H6 is, however, stronger than for H2 at the same dosage, although the delay of the peak of the heat production is the same or longer (from ca. 1 to ca. 5 hours). Also for this biopolymer, a continued heat production with time is observed compared to the end of heat production without biopolymers. However, whereas for H2 a 0.1 wt.% dosage had (hardly) no effect, the effect of this dosage is already large for H6. In terms of hardening and cumulative heat flow, the optimum dosage for H6 seems to lay between 0.1 and 0.25 wt.%, rather than 0. 25 wt.% for H2. At the end of the test, a lower total heat has been produced than for H2 (at 60 hour 45 J/g for 0.1 wt.% H6 versus 60 J/g solid at 0.25 wt.% H2).

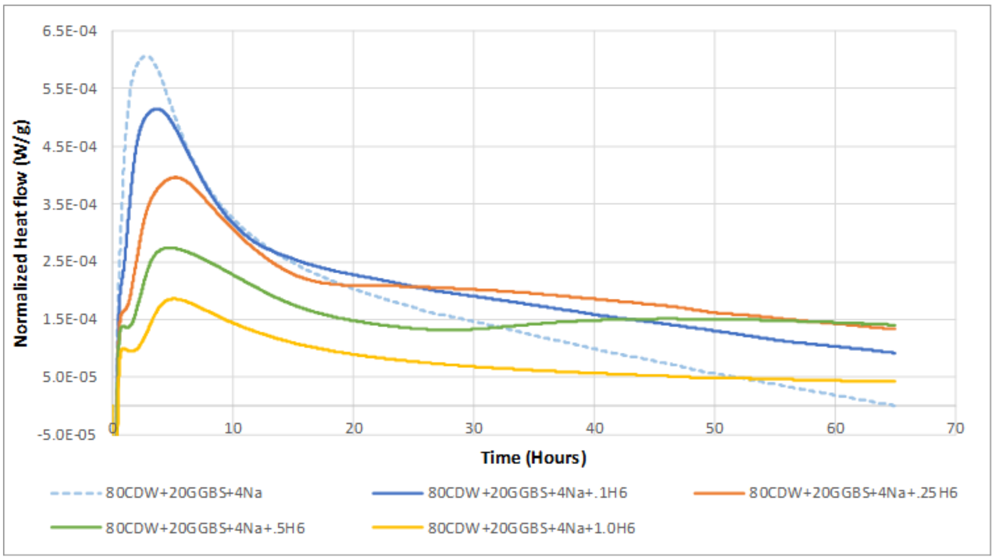


Figure 4.12 Normalized heat flow, samples with 80 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H6 content.

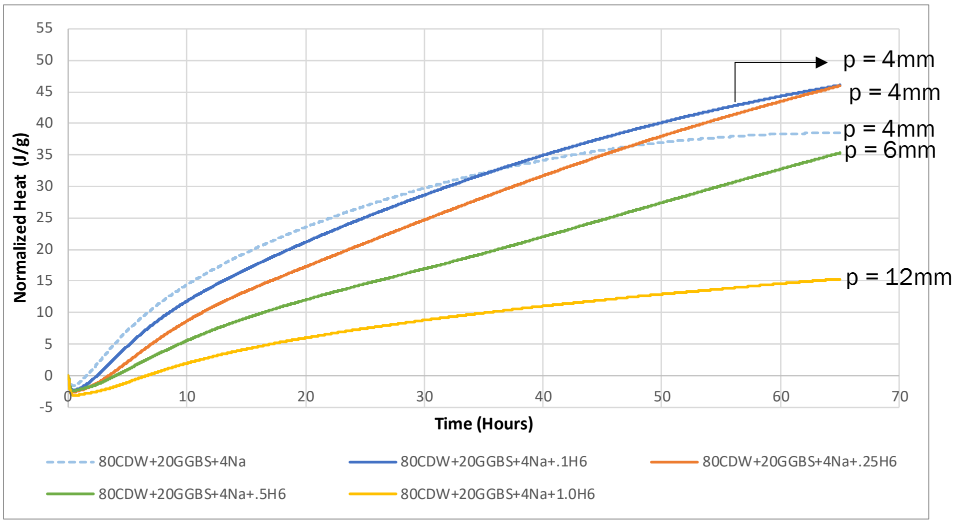


Figure 4.13 Normalized heat, samples with 80 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H6 content with needle penetration (p) at a heigh fall of 30 mm.

For the mixes with H7 (Figure 4.14 and Figure 4.15), the effect of dosage seems to be even more pronounced. At 1 wt.% H7, basically no peak is present and the delay of the (successively) smaller peak also seems to increase with dosage. The results at 0.1 wt.% H7, the results is, however, comparable to that of 0.1 wt-% H6 at the end of the test. The major difference between the two biopolymers H6 and H7 is that the degree of substitution after carbomethylation in H7 is higher than for H6 (DS = 0.37 versus 0.12).

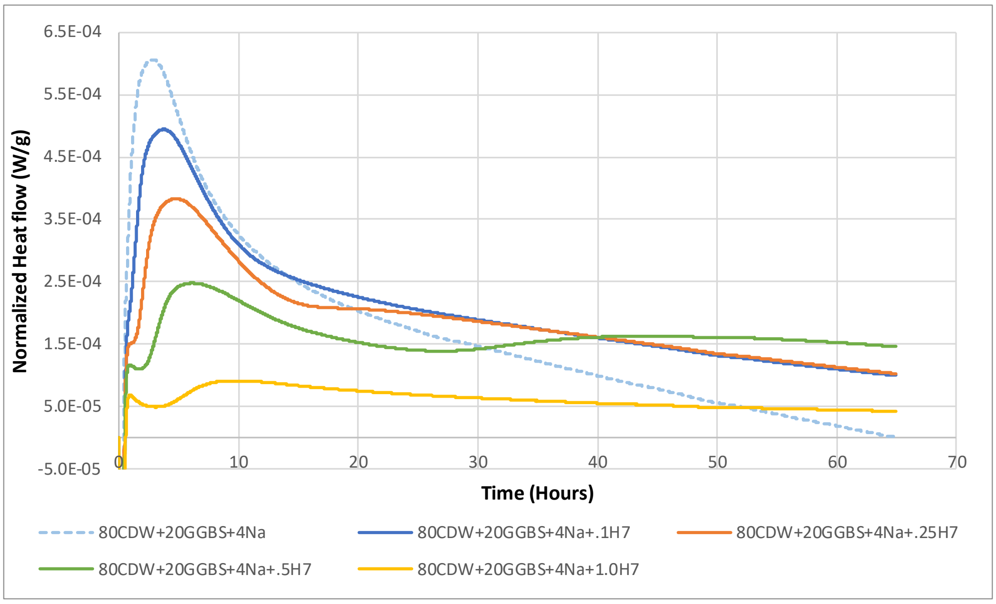


Figure 4.14 Normalized heat flow, samples with 80 CDW_MX + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H7 content.

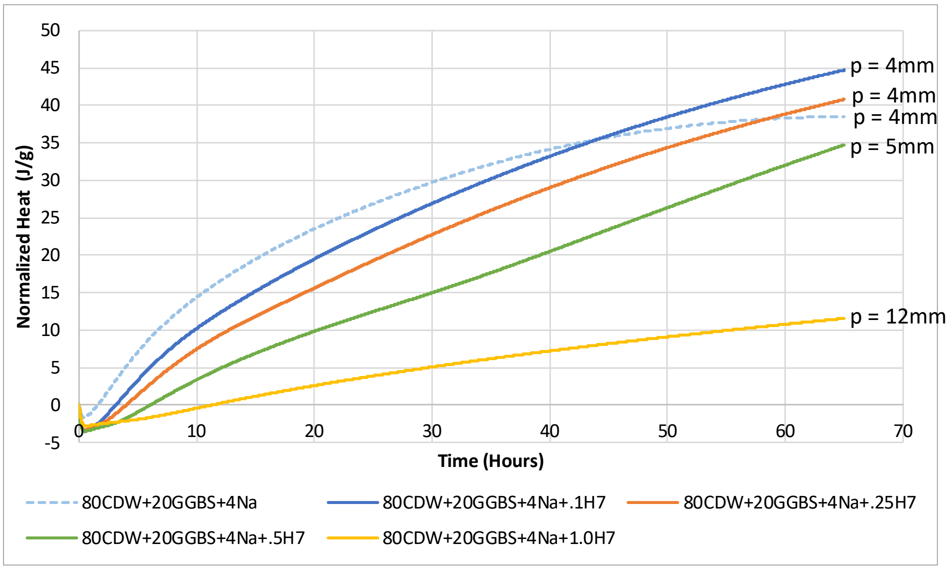


Figure 4.15 Normalized heat, samples with 80 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H7 content and needle penetration (p) at a heigh fall of 30 mm.

Mixes with biopolymer H9 (oxidized biopolymer with DO = 0.12) (Figure 4.16 and Figure 4.17) show, in addition to the reduced and delayed maximum normalized heat flow, also a period at the start of the test in which the heat production is greatly reduced. This reduction and the period over which it occurs become longer with higher dosages. Overall, however, the effect of the oxidized biopolymer is similar to the carbomethylated biopolymers. The result for biopolymer H10 (Figure 4.18 and Figure 4.19) and H11 (Figure 4.20 and Figure 4.21) show similar trends.

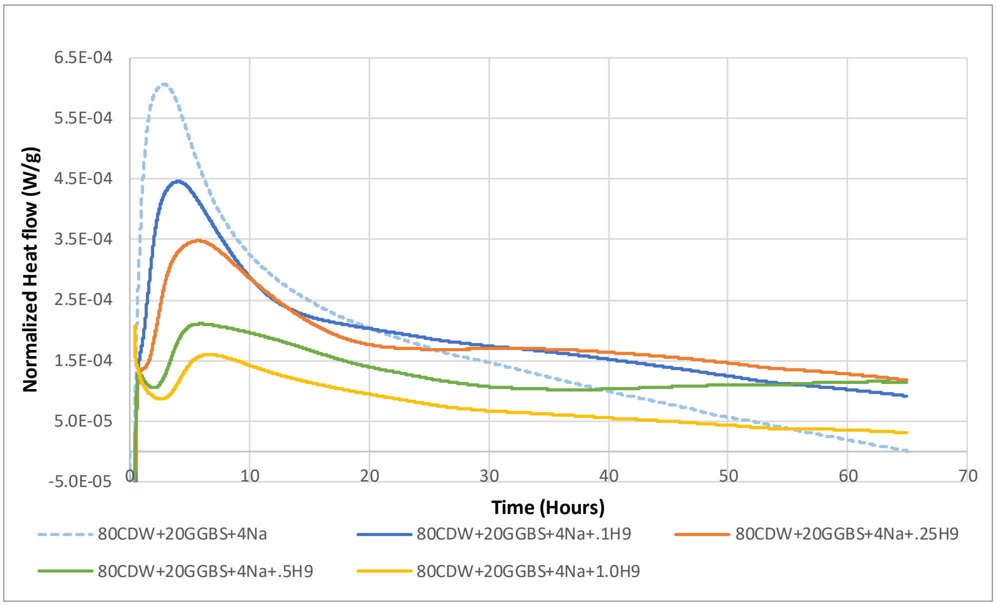


Figure 4.16 Normalized heat flow, samples with 80 CDW_MX + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H9 content.

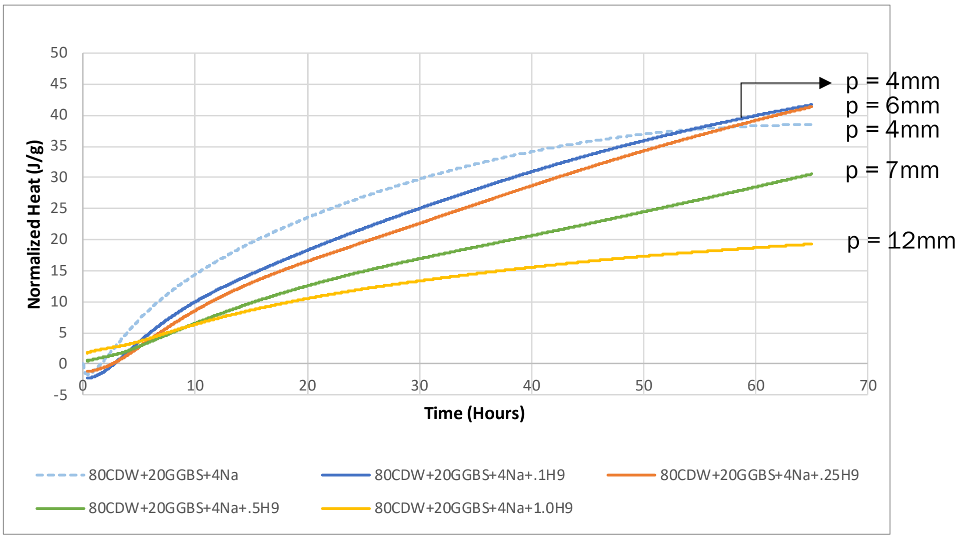


Figure 4.17 Normalized heat, samples with 80 CDW_MX + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H9 content with needle penetration (p) at a heigh fall of 30 mm.

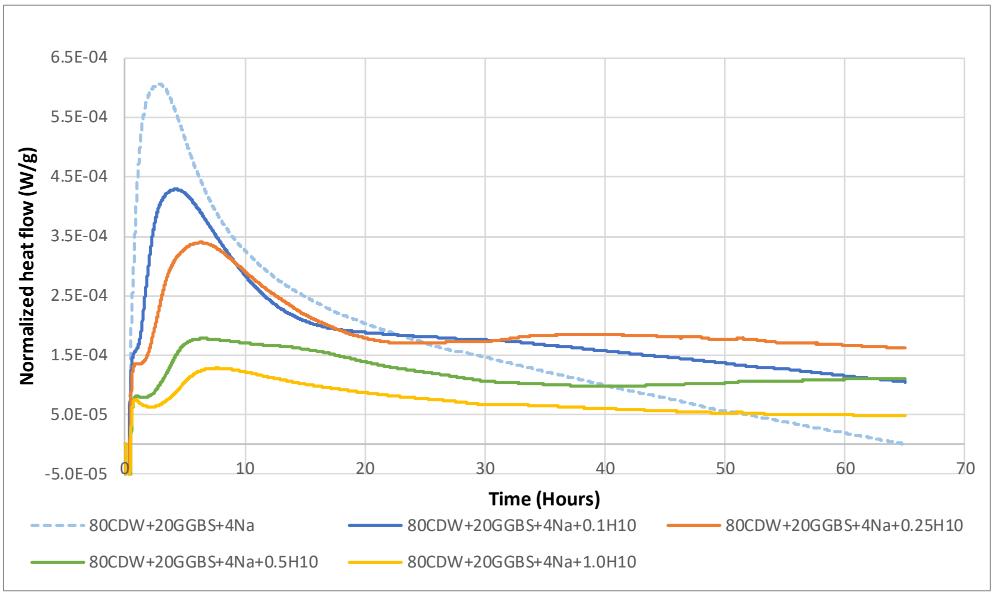


Figure 4.18 Normalized heat flow, samples with 100 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H10 content.

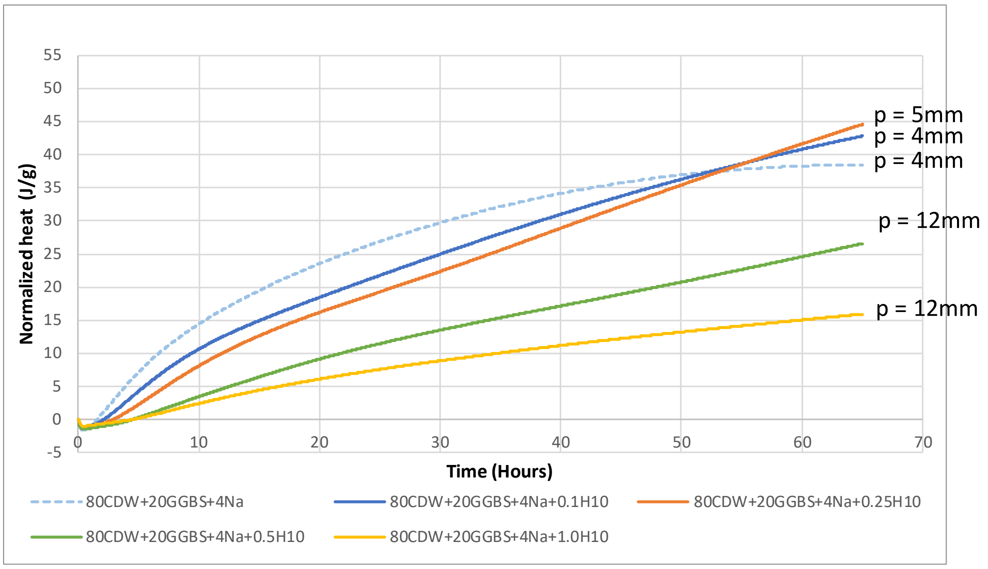


Figure 4.19 Normalized heat, samples with 80 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H10 content with needle penetration (p) at a heigh fall of 30 mm.

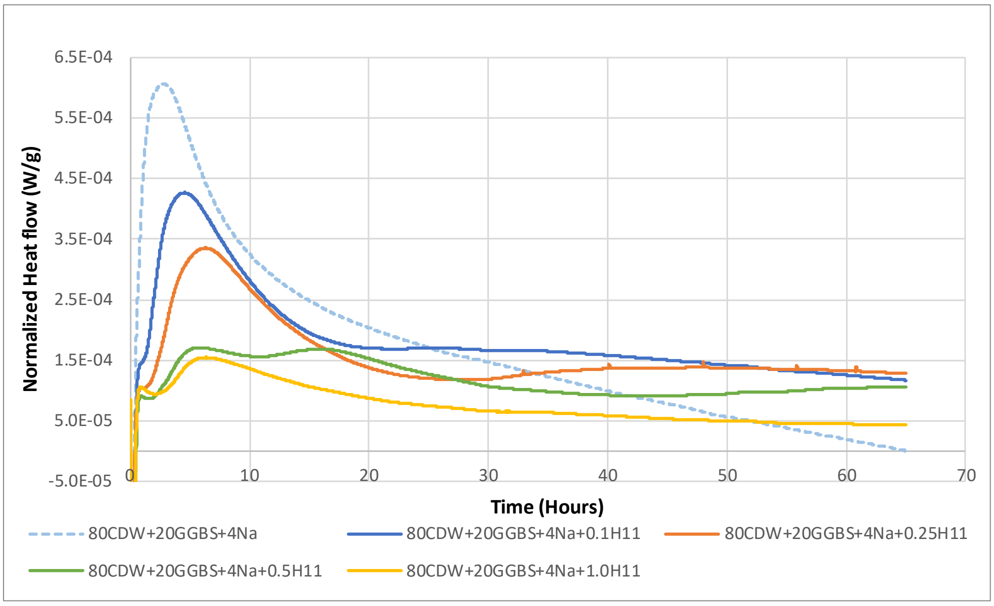


Figure 4.20 Normalized heat flow, samples with 100 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H11 content.

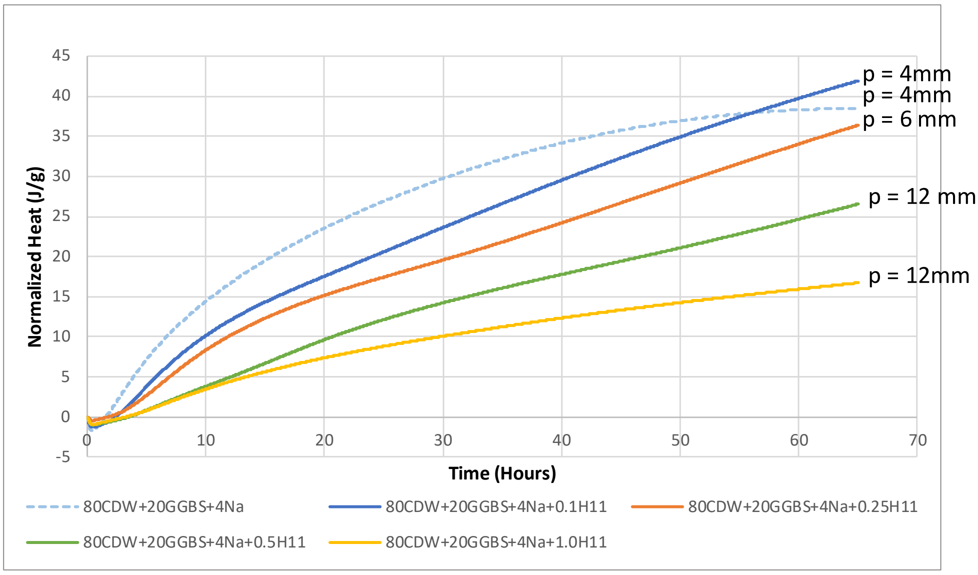


Figure 4.21 Normalized heat, samples with 80 CDW + 20 GGBS + 4% Na_2SO_4 and variation of biopolymer H11 content with needle penetration (p) at a heigh fall of 30 mm.

4.2.3 Summary of the results

As summary of the results of the microcalorimetry tests, Figure 4.22 shows the penetration depths after ca. 2.5 day in the microcalorimetry test from a fall height of 30 mm and Figure 4.23 the normalized heat flow as a function of dosage and type of the biopolymers. Figure 4.22 shows that the biopolymers delay the hardening with increasing dosages, from 0.1 wt.% onwards, although not at the same rate. Moreover, at 1 wt.%, no hardening at all occurs for all biopolymers, except for the unmodified one, H2. H2 is also the biopolymer that after 64 hours still shows ongoing heat development (Figure 4.23), indicating that it is likely that the hardening is still proceeding.

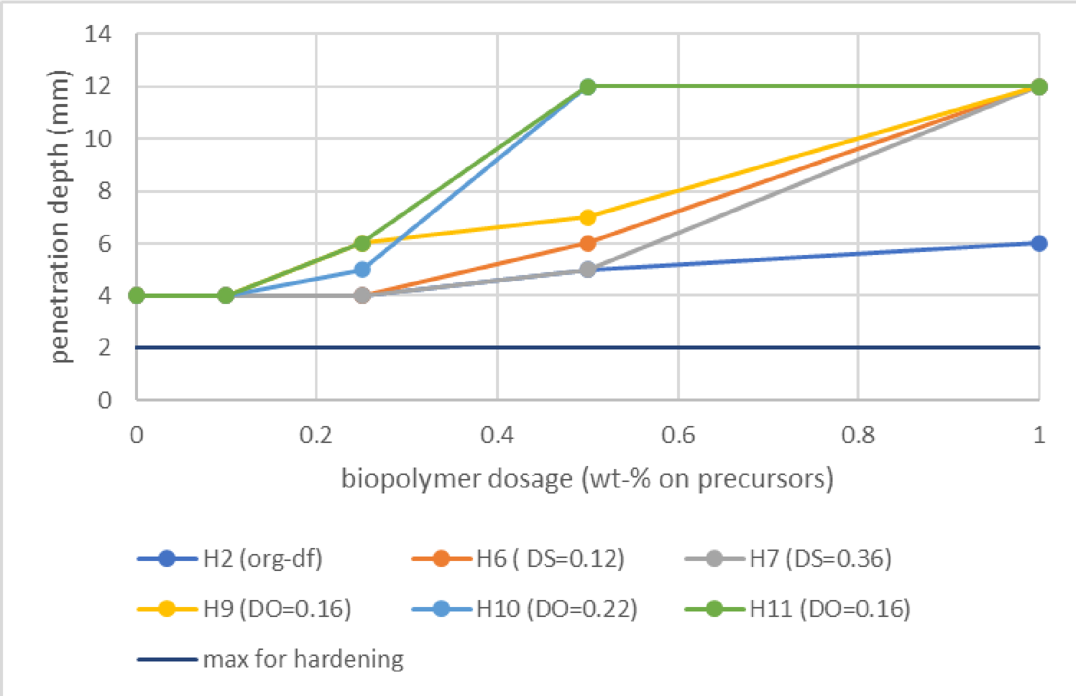


Figure 4.22 Penetration depths of the Vicat needle at a 30 mm fall height after 2.5 day of microcalorimetry test of the 80 CDW + 20 GGBS + 4% Na_2SO_4.

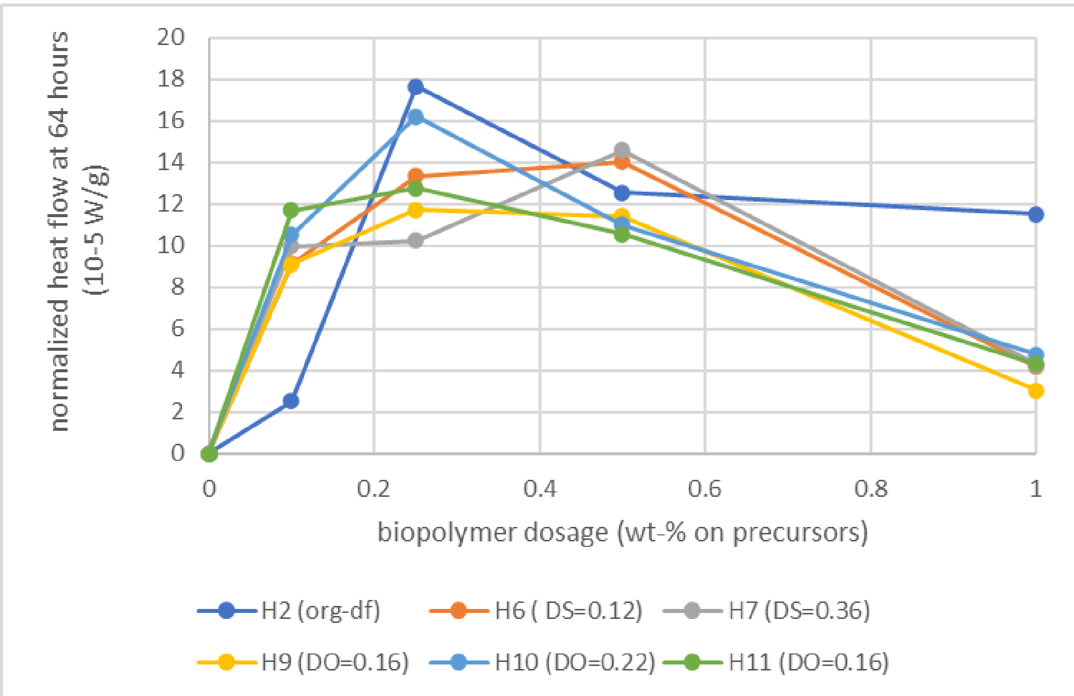


Figure 4.23 Normalized heat flow after 2.5 days of microcalorimetry test of the 80 CDW + 20 GGBS + 4% Na_2SO_4.

4.3 Mechanical properties

Figure 4.24and Figure 4.25 present the compressive and bending strength of the mortar bars with CDW_MX. Initially, the strength of the mortars was intended to be measured at 1 day, but at that age the samples were not fully hardened yet and could not be demoulded. All mixtures did, however, develop strength, although not very fast. Despite the high amount of heat developed in the microcalorimetry test, the compressive and bending strength of the mix with biopolymer H2 (unmodified biopolymer), is the lowest of the four mixes tested. For the carbomethylated biopolymer H6 and the oxidized biopolymer H10, the strengths are higher than for the mix without biopolymer.

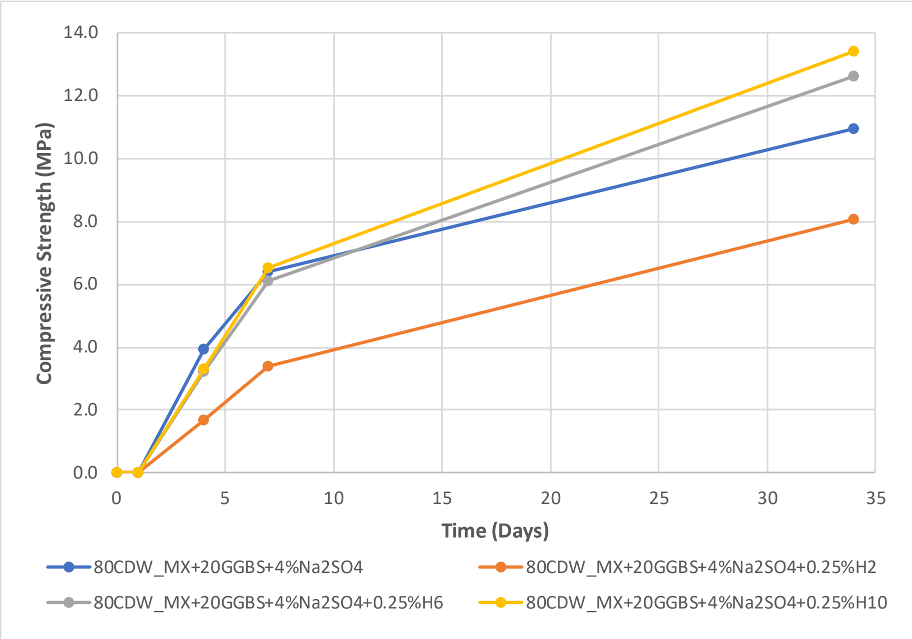


Figure 4.24 CDW_MX mortar mixes. Compressive strength vs. time.

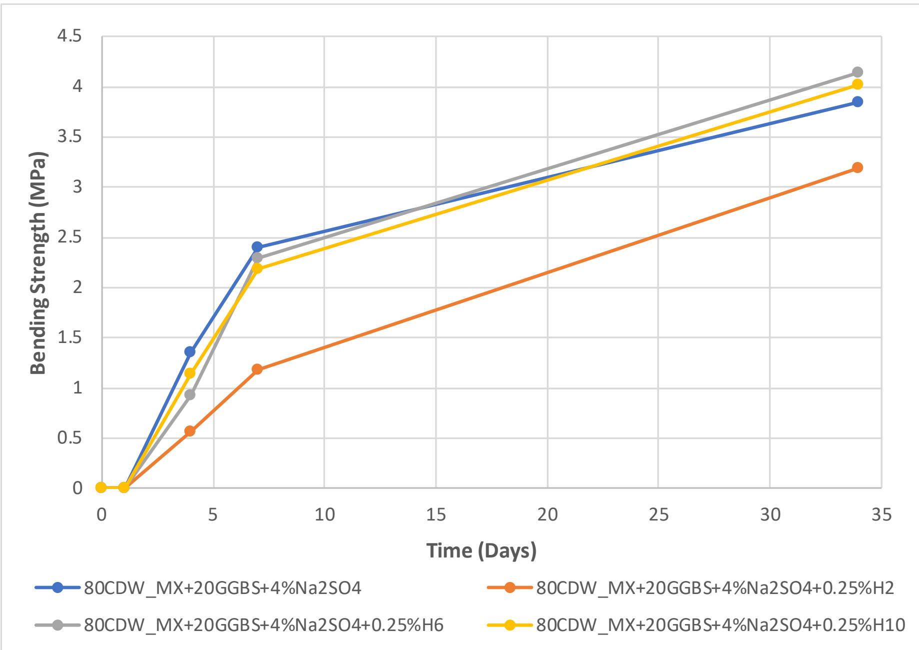


Figure 4.25 CDW_MX mortar mixes. Bending strength vs. time.

At 34 days, mortars with biopolymers H6 and H10 have a 15 % and 22 % higher compressive strengths than the reference without biopolymer. For the bending strength, this is 7 % and 4 %, respectively. At all the ages, the mix with the unmodified biopolymer H2 has the lowest strengths.

5 Results for CDW_SLP

5.1 Quick scan hardening test on paste

For CDW_SLP, different additives were tested for hardening up to 29 days. The samples that did not show any hardening after 9 days (Full needle penetration, 11 mm, at h = 0 mm) were discarded, except the reference mix that was tested until the end of the measurements. Table 5.1 shows which mixes were tested until 29 days and which were discarded at 9 days.

Table 5.1: Overview of mixes with CDW-SLP and various additives in the quick scan analyses for CDW_SLP.

Mix No.	Percentage of additives used by mass of CDW_SLP – W/B = 0.45					Discarded?
	Na_2SO_4	$CaSO_4$	NaOH	H6	H10	
Reference	-	-	-	-	-	NO
17 – 19	1%, 2% and 4%					NO
20 – 22		1%, 2% and 4%				Only 4%
23 – 25			1%, 2% and 4%			ALL
26 – 28	1%, 2% and 4%		1%			NO
29 – 31		1%, 2% and 4%	1%			Only mix with 4% $CaSO_4$
32 – 34	1%, 2% and 4%		4%			NO
35 - 37		1%, 2% and 4%	4%			Only mix with 4% $CaSO_4$
38				0.25%		YES
39					0.25%	YES
40	4%			0.25%		YES
41	4%				0.25%	YES
42		4%		0.25%		YES
43		4%			0.25%	YES
44			4%	0.25%		YES
45			4%		0.25%	YES

It can be seen in the table that CDW-SLP without any additives does not harden within 9 days. The same applies for CDW_SLP with 4 % $CaSO_4$ and the mixes with NaOH or biopolymers H6 and H10 when using these additives individually. Combining either H6 with NaOH or H10 with NaOH also does not have an effect on hardening.

5.1.1 The reference: CDW_SLP without additives

In Figure 5.1, it can be seen that the reference mix hardens between 11 and 14 days (the two measuring moments), but only for zero impact load (needle height = 0 mm). At a needle height of 10 mm, some resistance against the needle penetration occurs after 14 days, but for a needle drop from 30 mm, no resistance is build up to 29 days, indicating that no sufficient hardening takes place.

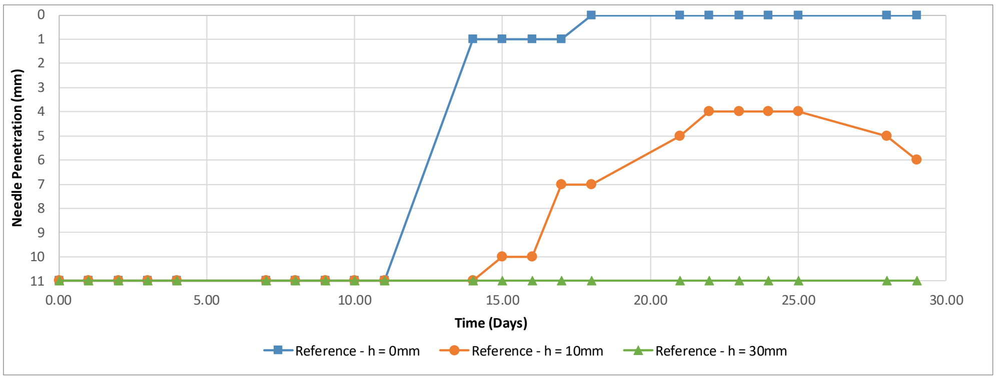


Figure 5.1 Needle penetration Reference (CDW_SLP without additives) at h =0, 10 and 30 mm.

The figure shows that the mix reaches an initial cohesion at 14 days, when at h = 0 mm, the needle penetrates only 1 mm. For h = 10 mm, needle penetration after 25 days increases again as if the samples was weakening again. A reason for this can be that the sample was subject to hardening by drying (false hardening). As explained before, this phenomenon can overestimate the hardening of the samples. Once the samples are wetted, the effect of the drying is gone and the real binding capacity can be measured again. For h = 30 mm, the needle penetration has always reached the maximum.

5.1.2 CDW_SLP + 1, 2 or 4% Na_2SO_4

Figure 5.2 to Figure 5.4 show the results for the needle penetration at a drop height of h = 0 mm, h = 10 mm and h = 30 mm, respectively. The mixes presented have Na_2SO_4 contents of 1%, 2% and 4%. The results of the reference mix are shown for comparison.

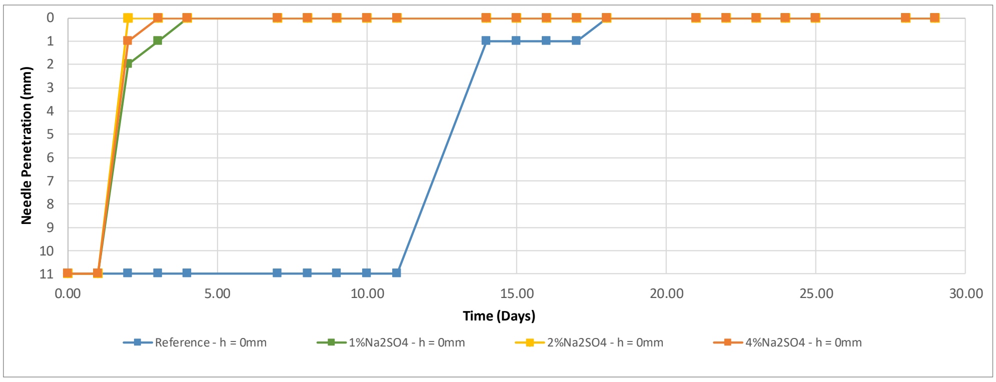


Figure 5.2 Needle penetration Reference (CDW_SLP without additives) and CDW_SLP + 1, 2 or 4% Na_2SO_4 – h = 0 mm.

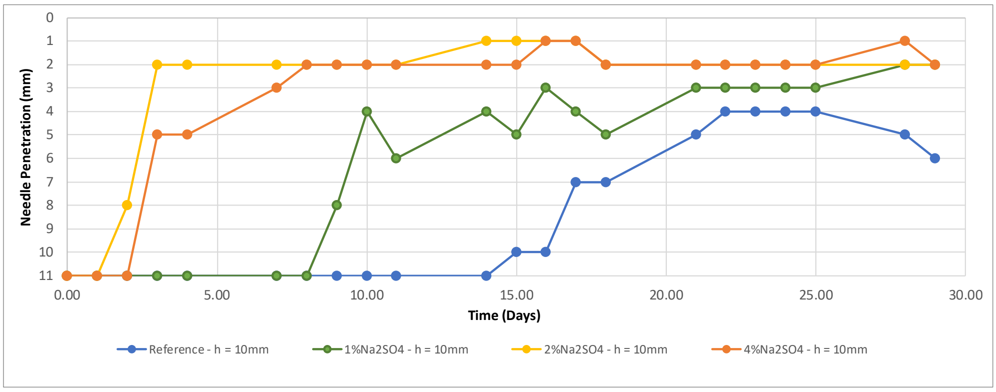


Figure 5.3 Needle penetration CDW_SLP + 1, 2 or 4% Na_2SO_4 – h = 10 mm.

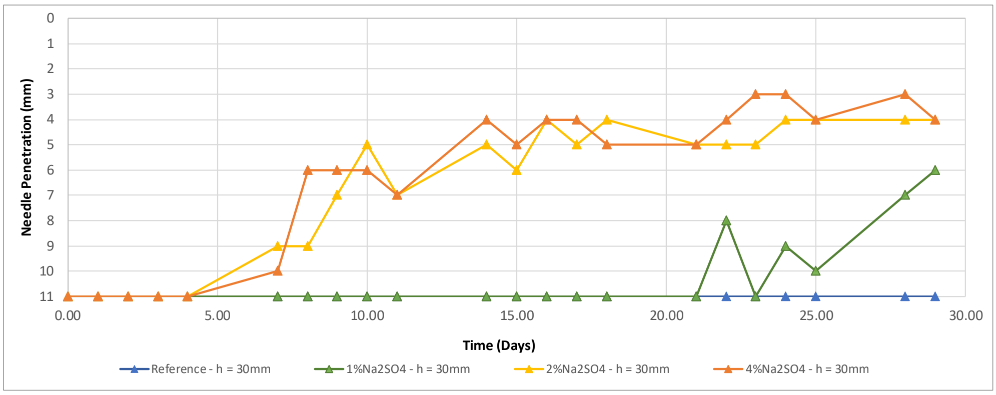


Figure 5.4 Needle penetration CDW_SLP + 1, 2 or 4% Na_2SO_4 – h = 30 mm.

At h = 0 mm, after 4 days all the mixes with Na_2SO_4 show a needle penetration of 0 mm. For the other needle drop heights, the mixes with 2 % and 4 % Na_2SO_4 perform similarly and reach a lower needle penetration at early ages in comparison with the mix of 1 % Na_2SO_4. In comparison with the reference mix, the mixes with Na_2SO_4 harden faster and develop higher binding properties. Nonetheless, after 29 days at a needle drop height of h=30 mm, none of the mixes reached a penetration of maximum 2 mm, which indicates the final hardening of the paste.

5.1.3 CDW_SLP + 1 % Na_2SO_4 + 0, 1 or 4% NaOH

Figure 5.5 to Figure 5.7 show the results for the needle penetration at a drop height of h = 0 mm, h = 10 mm and h = 30 mm, respectively. The mixes presented have a fix content of 1 % Na_2SO_4 and NaOH contents of 0, 1 or 4 %. The reference mix and the mix with 1% Na_2SO_4 without NaOH are shown for comparison.

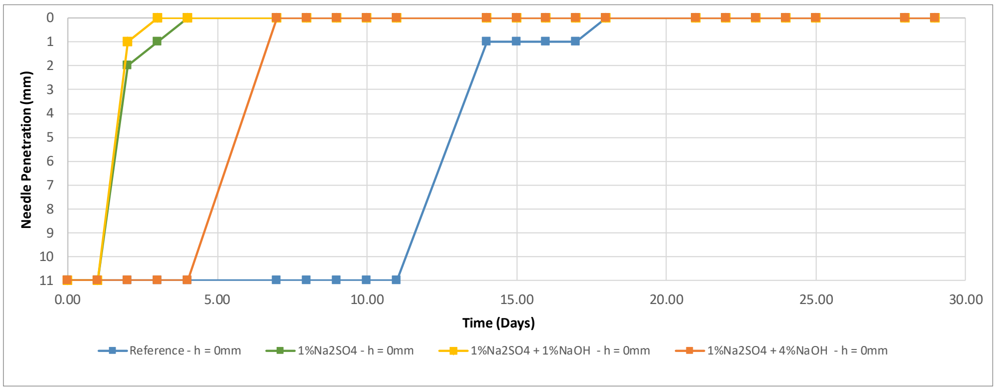


Figure 5.5 Needle penetration CDW_SLP + 1% Na_2SO_4 + 1 or 4% NaOH – h = 0 mm.

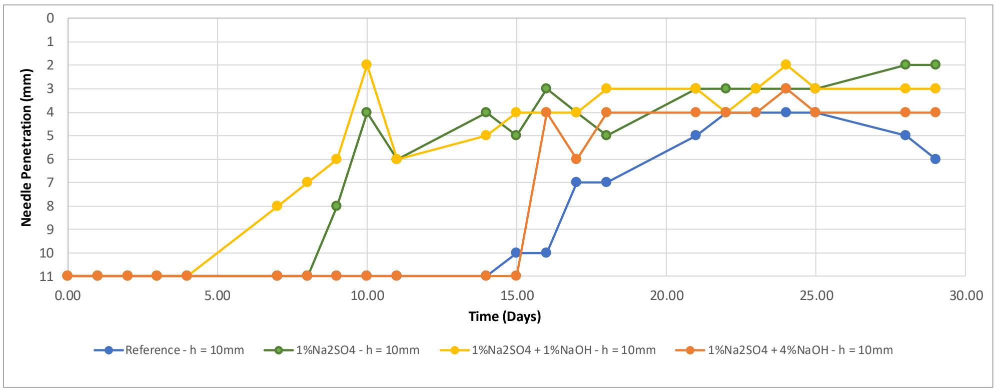


Figure 5.6 Needle penetration CDW_SLP + 1% Na_2SO_4 + 1 or4% NaOH – h = 10 mm.

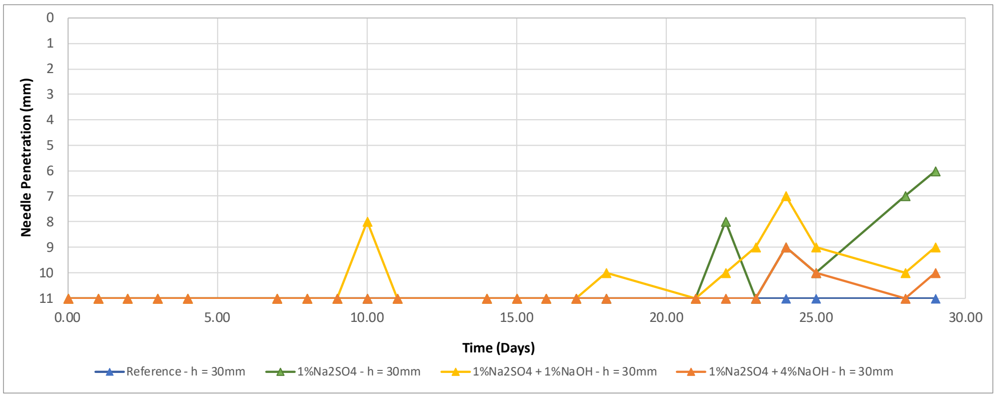


Figure 5.7 Needle penetration CDW_SLP + 1% Na_2SO_4 + 1 or 4% NaOH – h = 30 mm.

At a needle drop height of 0 mm, the mix without NaOH reaches a penetration of 0 mm at 4 days, the one with 1 % NaOH at 3 days and the one with 4 % NaOH at 7 days. For the needle drop height of 10 and 30 mm, after 29 days, the mix without NaOH reaches a lower needle penetration than the mixes with NaOH. Overall, the mixes with only Na_2SO_4 perform better than the mixes with NaOH. However, after 29 days at a needle drop height of 30mm, none of the mixes reaches a penetration of at least 2 mm which indicates the final hardening of the paste.

At 10 and 24 days for drop height of 10 and 30 mm, there is a peak in the needle penetration depth. Between 10 and 24 days, the samples reach certain degree of hardening, but at higher age, they apparently soften again. This phenomenon can be due to two main factors. As mentioned in the section on experimental procedure, the samples are wetted when the surface looks dry to prevent that the hardening is happening due to capillary tension instead of development of the binding properties. It is possible that the apparent optimum is due to drying hardening and that, after the samples have been wetted again, they went back to a state without capillary tension. The other reason, although less likely, is that there might be issues with the mixing of the samples and small harder lumps occur that block the needle, thus overestimating the hardening of the material.

5.1.4 CDW_SLP + 2 % Na_2SO_4 + 0, 1 or 4% NaOH

Figure 5.8 to Figure 5.10 show the results for the needle penetration at a drop height of h = 0 mm, h = 10 mm and h = 30 mm, respectively. The mixes presented have a fix content of 2% Na_2SO_4 and NaOH contents of 0, 1 and 4%. The reference mix and the mix with 2% Na_2SO_4 without NaOH] are shown for comparison.

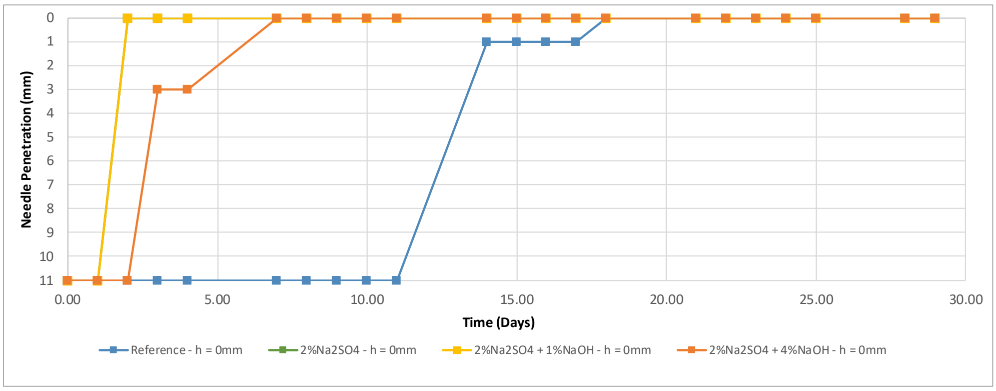


Figure 5.8 Needle penetration CDW_SLP + 2% Na_2SO_4 + 1 or 4% NaOH – h = 0 mm.

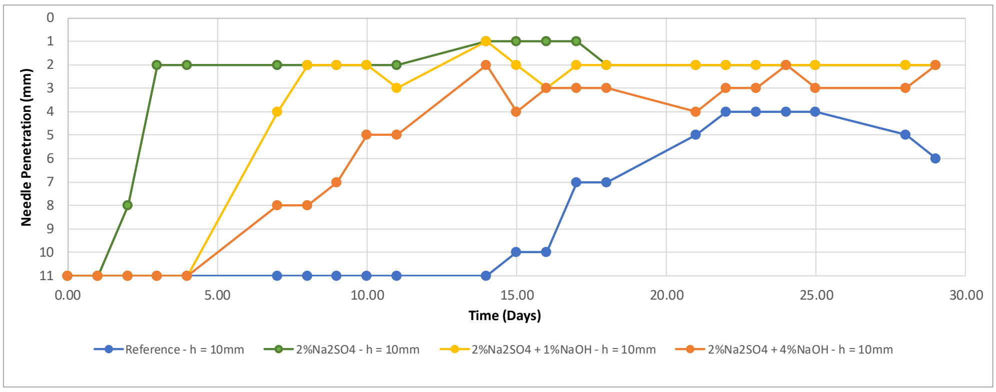


Figure 5.9 Needle penetration CDW_SLP + 2% Na_2SO_4 + 1 or 4% NaOH – h = 10 mm.
]

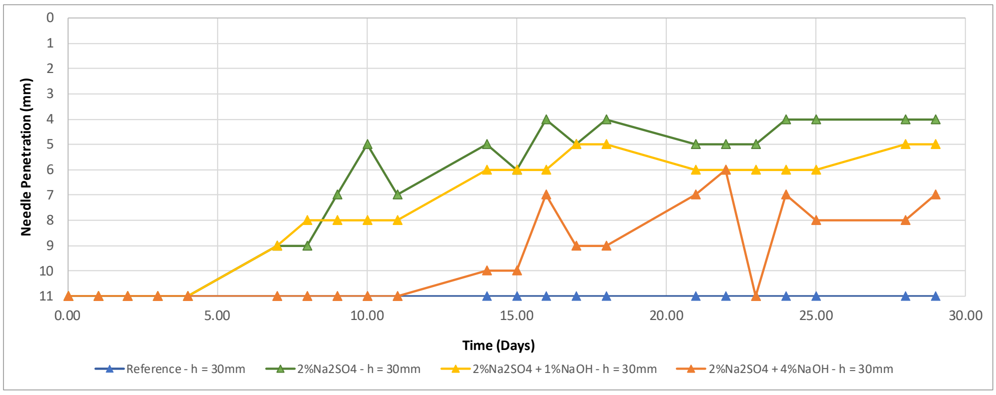


Figure 5.10 Needle penetration CDW_SLP + 2% Na_2SO_4 + 1 or 4% NaOH – h = 30 mm.

Comparing the mixes with 2% Na_2SO_4 and NaOH, the mix without NaOH performs best, similar to the mixes with 1% Na_2SO_4. As for the previous mixes, after 29 days none of the mixes reach a maximum needle penetration of 2 mm from a needle drop high of 30 mm.

5.1.5 CDW_SLP + 4% Na_2SO_4 + 0, 1 or 4% NaOH

Figure 5.11 to Figure 5.13 show the results for the needle penetration at a drop height of h = 0 mm, h = 10 mm and h = 30 mm, respectively. The mixes presented have a fix content of 4 % Na_2SO_4 and NaOH contents of 0, 1 and 4 %. The reference mix and the mix with 4 % Na_2SO_4 without NaOH are shown for comparison.

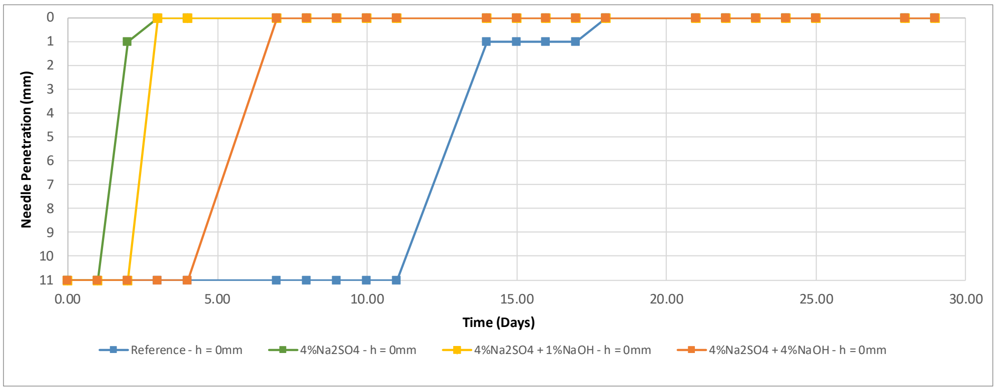


Figure 5.11 Needle penetration CDW_SLP + 4% Na_2SO_4 + 1 or 4% NaOH – h = 0 mm.

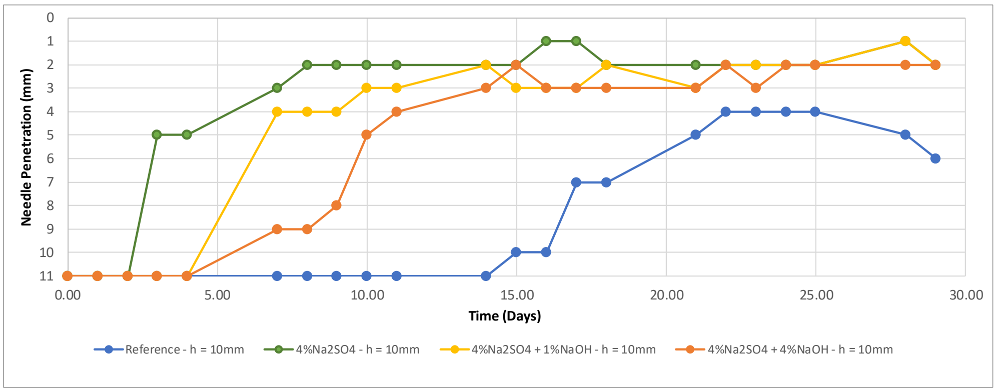


Figure 5.12 Needle penetration CDW_SLP + 4% Na_2SO_4 + 1 or 4% NaOH – h = 10 mm.

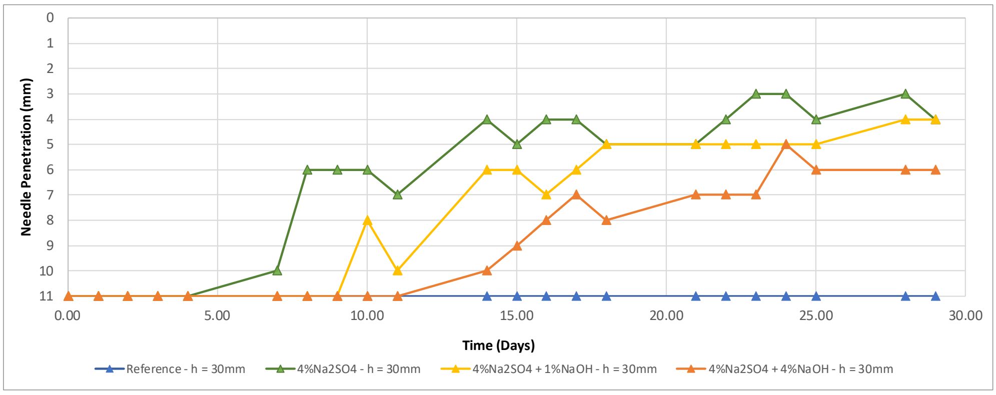


Figure 5.13 Needle penetration CDW_SLP + 4% Na_2SO_4 + 1 or 4% NaOH – h = 30 mm.

The results obtained are similar as for the mixes with 1 and 2% Na_2SO_4 with NaOH: the mix with only 4%Na_2SO_4 without NaOH performs the best. As for the previous mixes, after 29 days none of the mixes reach a maximum needle penetration of 2 mm from a needle drop high of 30 mm.

5.1.6 CDW-SLP + 1 or 2% $CaSO_4$

Figure 5.14 to Figure 5.16 show the results for the needle penetration at a drop height of h = 0 mm, h = 10 mm and h = 30 mm, respectively. The mixes presented have $CaSO_4$ contents of 1 and 2%. The reference mix and the mix with 4% $CaSO_4$ (until 9 days) are shown for comparison.

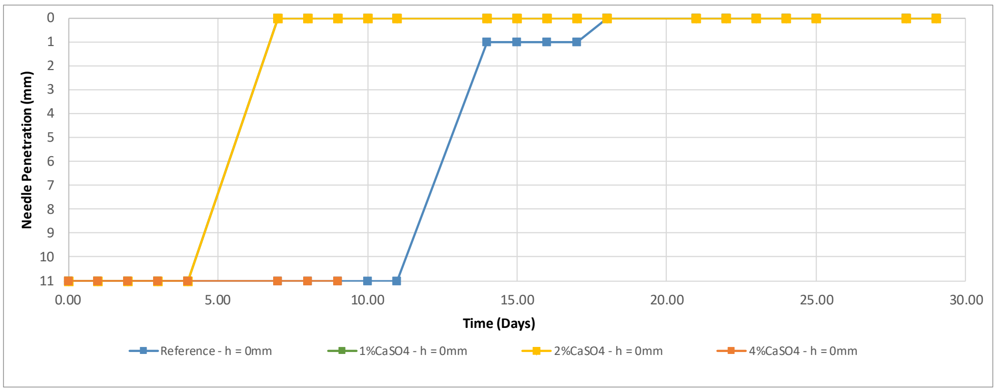


Figure 5.14 Needle penetration CDW_SLP + 1, 2 or 4 % $CaSO_4$ – h = 0 mm.

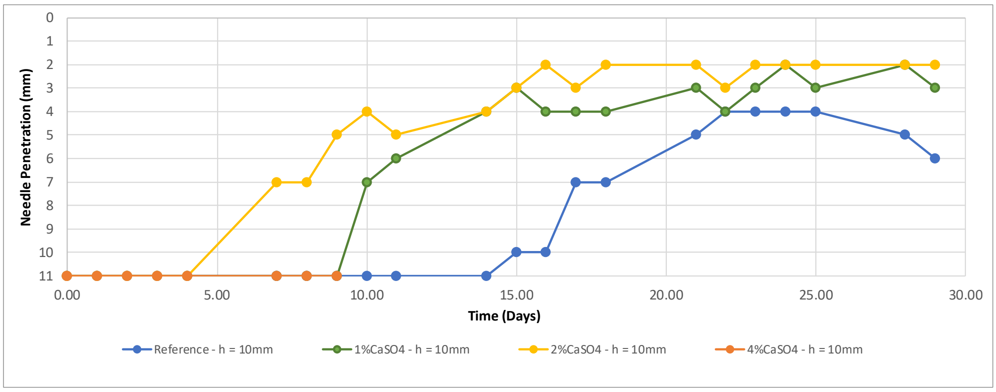


Figure 5.15 Needle penetration CDW_SLP + 1, 2 or 4% $CaSO_4$ – h = 10 mm.

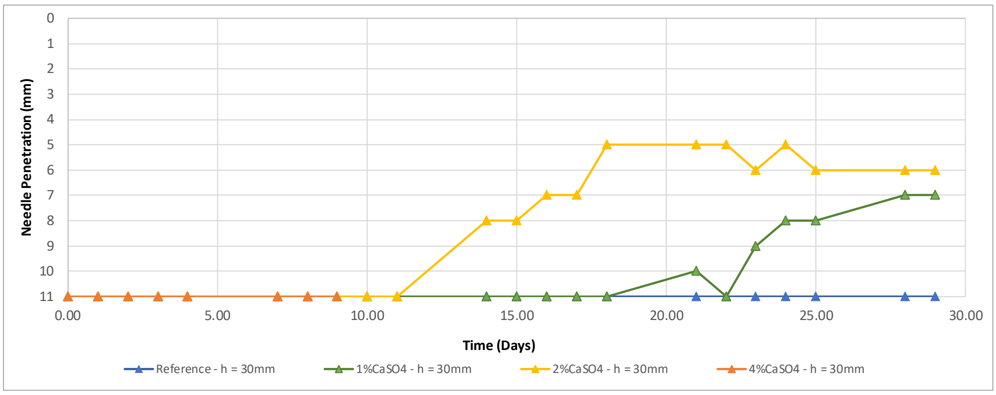


Figure 5.16 Needle penetration CDW_SLP + 1, 2 or 4% $CaSO_4$ – h = 30 mm.

The mix with 2% $CaSO_4$ performs better than the mix with 1% $CaSO_4$, presenting lower needle penetration at earlier ages. Nonetheless, as for the previous mixes, after 29 days none of the mixes reach a maximum needle penetration of 2 mm from a needle drop high of 30 mm.

5.1.7 CDW-SLP + 1% $CaSO_4$ + 0, 1, 4% NaOH

Figure 5.17 to Figure 5.19 show the results for the needle penetration at a drop height of h=0mm, h=10mm and h = 30mm respectively. The mixes presented have a fix content of 1% CaSO4 and NaOH contents of 0, 1 and 4%. The reference mix and the mix with 1% CaSO4 without NaOH are shown for comparison.

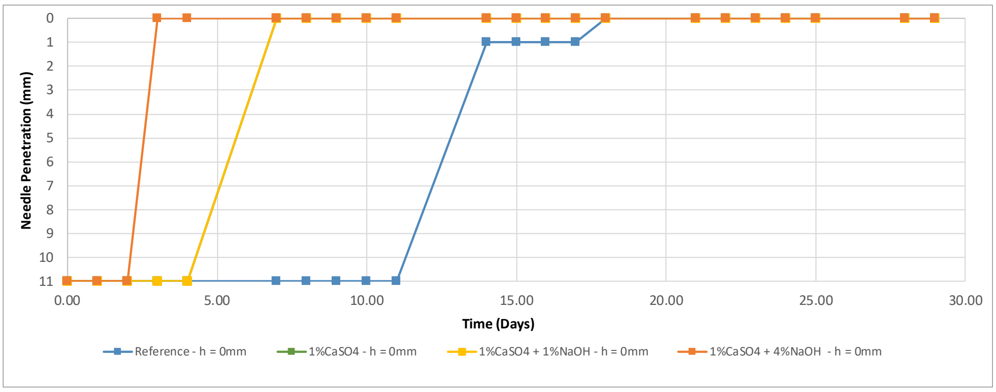


Figure 5.17 Needle penetration CDW_SLP + 1% $CaSO_4$ + 1 or 4% NaOH - h = 0 mm.

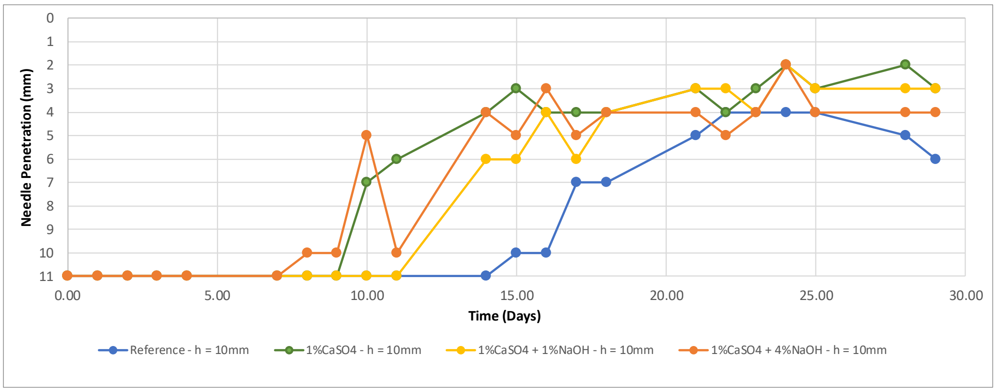


Figure 5.18 Needle penetration CDW_SLP + 1% $CaSO_4$ + 1 or 4% NaOH - h = 10 mm.

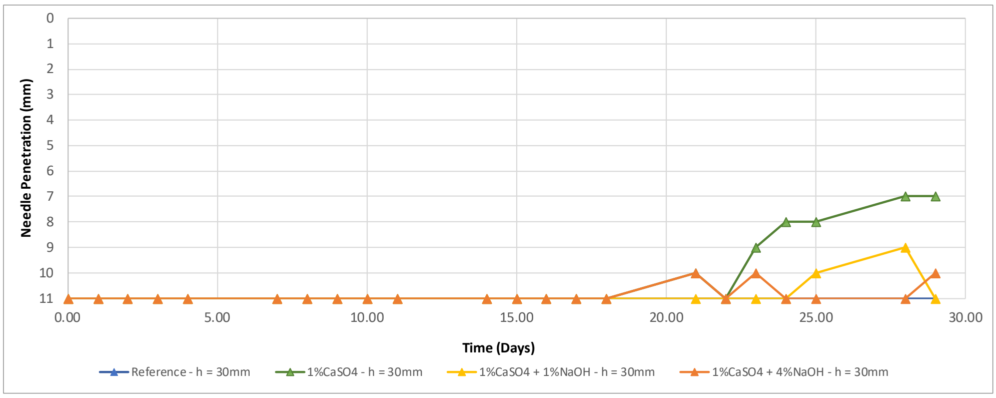


Figure 5.19 Needle penetration CDW_SLP + 1% $CaSO_4$ + 1 or 4% NaOH - h = 30 mm.

At the end of the measurements, for the needle drop heigh of 30 mm, the mix with only $CaSO_4$ obtained the lowest needle penetration in compared with those with $CaSO_4$ and NaOH. Nonetheless, as for the previous mixes, after 29 days none of the mixes reached a maximum needle penetration of 2 mm from a needle drop high of 30 mm.

5.1.8 CDW-SLP + 2% $CaSO_4$ + 0, 1 or 4% NaOH

Figure 5.20 to Figure 5.22 show the results for the needle penetration at a drop height of h = 0 mm, h = 10 mm and h = 30 mm, respectively. The mixes presented have a fix content of 2% $CaSO_4$ and NaOH contents of 0, 1 and 4%. The reference mix and the mix with 2% $CaSO_4$ without NaOH are shown for comparison.

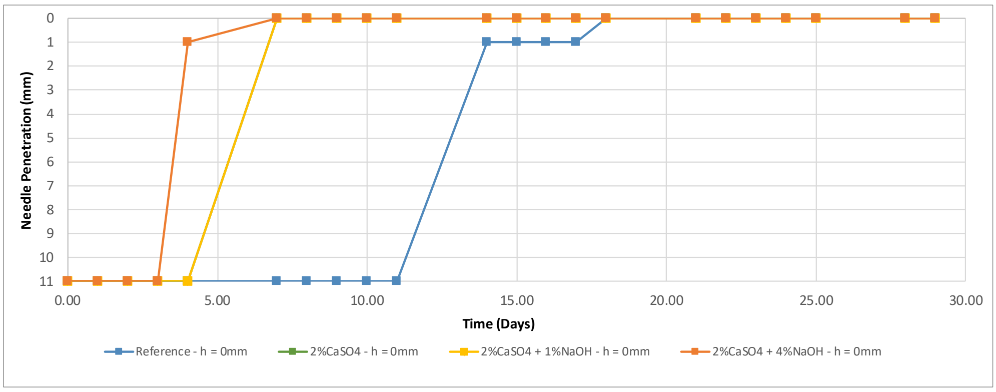


Figure 5.20 Needle penetration CDW_SLP + 2% $CaSO_4$ + 1 or 4% NaOH - h = 0 mm.

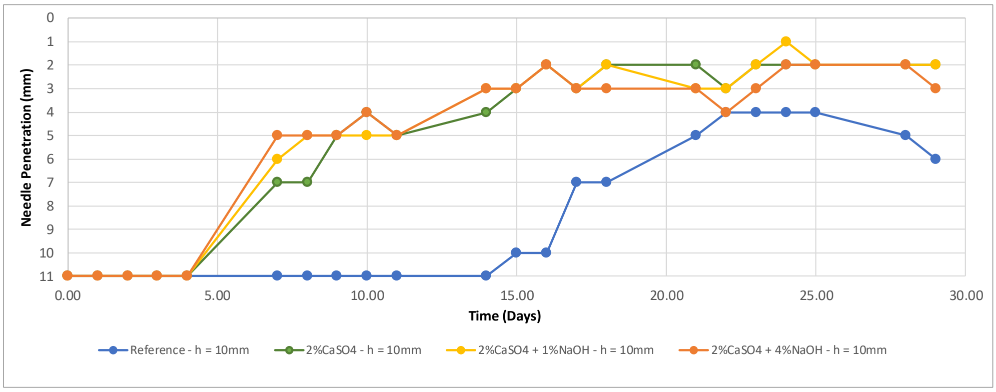


Figure 5.21 Needle penetration CDW_SLP + 2% $CaSO_4$ + 1 or 4 % NaOH - h = 10 mm.

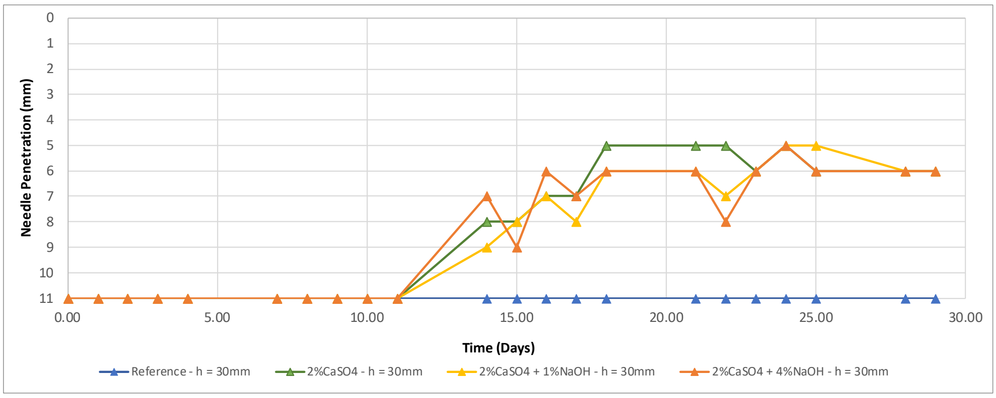


Figure 5.22 Needle penetration CDW_SLP + 2% $CaSO_4$ + 1 or 4% NaOH - h = 30 mm.

The results obtained are similar to the mixes with 1% $CaSO_4$ and NaOH. The mix with only $CaSO_4$ performed very similar to the other 2 mixes, showing that the NaOH has a low impact on the binding development. Nonetheless, as for the previous mixes, after 29 days none of the mixes reached a minimum needle penetration of 2 mm from a needle drop high of 30 mm.

5.1.9 Summary of the results

Table 5.2 presents the start and end of binding for h = 0 mm. The first is defined as the last day with less than the maximum needle penetration (11 mm), the second as the day at which the penetration is equal or lower than 2 mm. For h = 30 mm, the table indicates the first day at which the needle did not reach the maximum penetration, which is the day from which hardening can measured from this drop heigh.

Table 5.2: Summary hardening test of the mixes with CDW-SLP and various additives.

Mix	Percentage of inorganic additives used by mass of CDW_SLP – w/b = 0.45			h = 0 mm Start – End binding (Days)	h = 30 mm First day at which penetration < 11mm (Days)	Conclusion
	Na_2SO_4	$CaSO_4$	NaOH			
Reference				11 - 18	-	Not stiff, not hardened
17	1			2 - 4	24	Stiff, not hardened
18	2			2 - 2	7	id
19	4			2 - 3	7	id
20		1		7 - 7	23	id
21		2		7 - 7	14	id
26	1		1	2 - 3	22	id
27	2		1	2 - 2	7	id
28	4		1	3 - 3	10	id
29		1	1	7 - 7	29	Cohesive
30		2	1	7 - 7	14	Stiff, not hardened
32	1		4	7 - 7	29	Cohesive

33	2		4	3 - 7	14	Stiff, not hardened
34	4		4	7 - 7	14	Stiff, not hardened
35		1	4	3 - 3	29	Cohesive
36		2	4	4 - 7	14	Stiff, not hardened

The mixes with Na_2SO_4 and 0 or 1% NaOH have a similar start and end binding for h = 0 mm. For the Na_2SO_4 mixes with 4% NaOH, binding is delayed up to 3 days. The mixes with $CaSO_4$ and 0 or 1% NaOH also have a similar start and end binding for h = 0 mm. The mixes with 4% NaOH start binding at an earlier age whilst for the mix with 1% $CaSO_4$ binding ends earlier (3 days) than for the other $CaSO_4$ mixes. For h = 30 mm, the mixes with Na_2SO_4 faster reach initial hardening than the mixes with $CaSO_4$. Overall, NaOH does not accelerate the hardening process at h = 30 mm, regardless of the sulphate component. In contrast, in most cases except for the mix 2% Na_2SO_4 + 1 % NaOH, hardening is delayed.
Figure 5.23 presents a comparison of the needle penetration values at 29 days from h = 30 mm for the mixes with different contents of Na_2SO_4, NaOH and the combination of both. Similar data is presented in Figure 5.24 for the mixes with $CaSO_4$ and NaOH. In this case, it was assumed that after 29 days, the penetration of all the mixes with 4% CaSO4 was still 11 mm, same as the last measured data point at 9 days before discarding the mix. This is indicated with a dashed line.

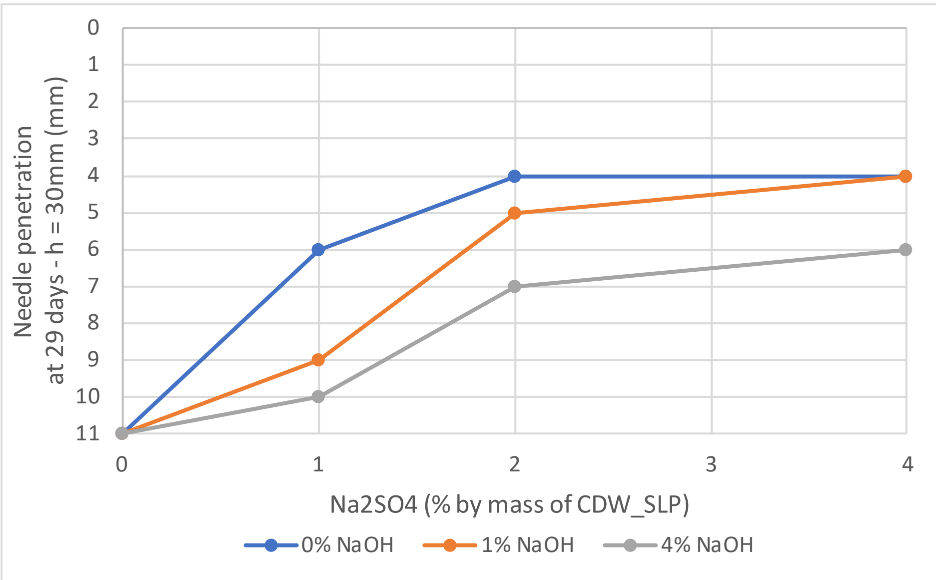


Figure 5.23 29 days needle penetration results for CDW_SLP with variations of Na_2SO_4 and 0, 1 or 4% NaOH - h = 30 mm.

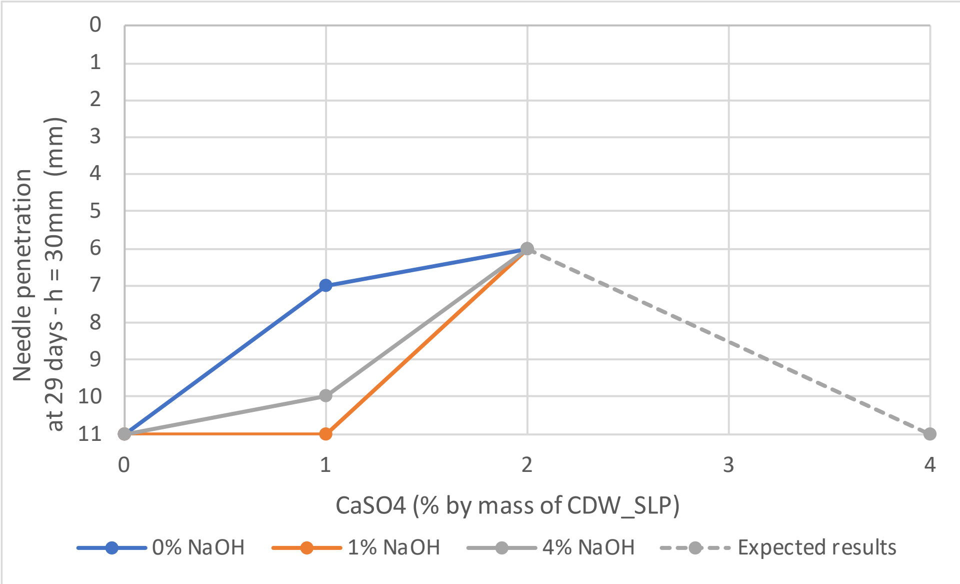


Figure 5.24 29 day needle penetration results for CDW_SLP + variations of CaSO4 + 0, 1 or 4% NaOH - h = 30 mm. Dashed line indicates expected values.

For the mixes with Na_2SO_4, the best result is the one with 2% without NaOH. As said before, the NaOH either hampers or does not influence the hardening of these mixes. For the $CaSO_4$ mixes, the best results are with 2% $CaSO_4$ regardless of the NaOH content. Therefore, it is also preferred not to use NaOH in these mixes. Based on hardening test, it was decided to use Na_2SO_4 instead of $CaSO_4$ for the mortar bars and to skip the use of NaOH.

5.2 Mechanical properties

Figure 5.25 and Figure 5.26 present the compressive and bending strength of the mortar bars with CDW_SLP. Initially, it was intended to determine the strength of the bars at 1 day, but the samples were not fully hardened and could not be demoulded.

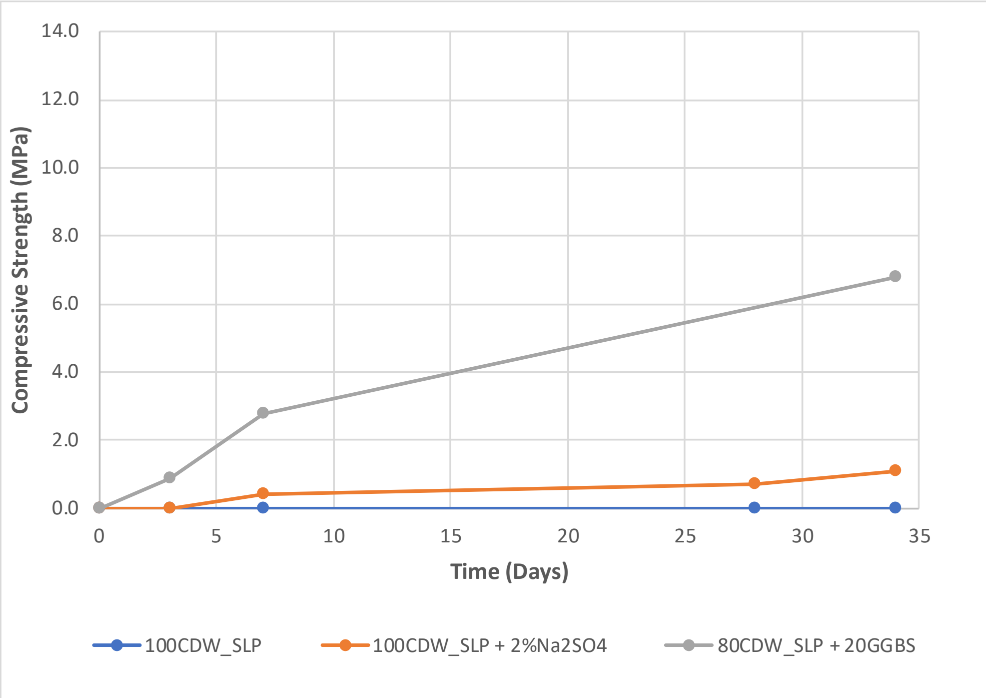


Figure 5.25 CDW_SLP mortar mixes, Compressive strength vs. time.

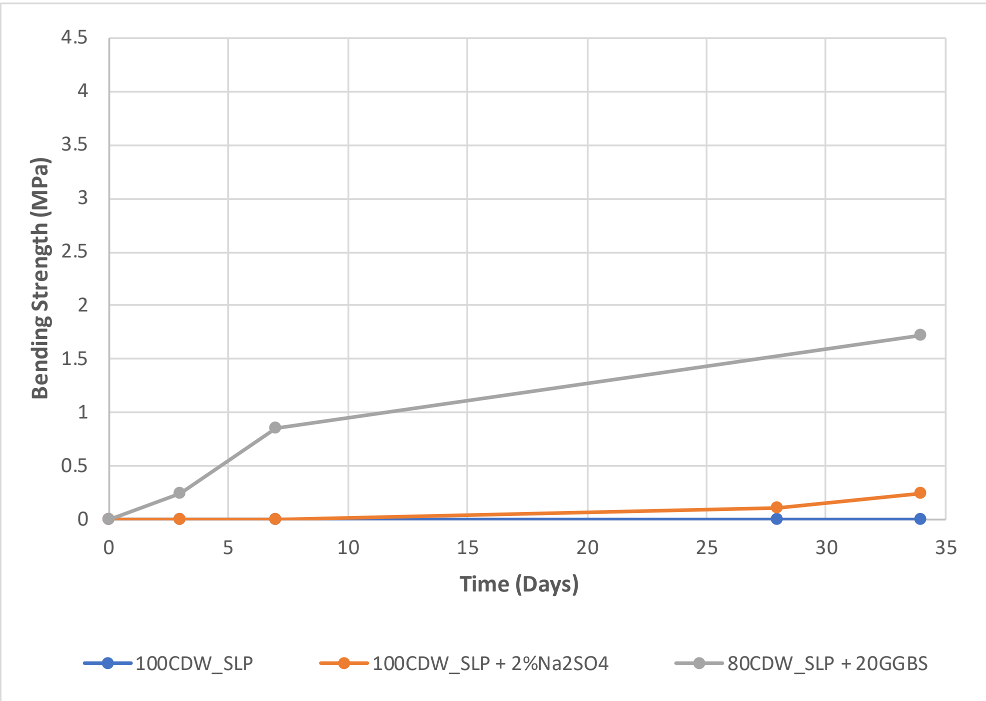


Figure 5.26 CDW_SLP mortar mixes, Bending strength vs. time.

The mixes with only CDW_SPL and with Na_2SO_4 performed similarly, having very low strengths. The mix with GGBS performed better but still has lower strengths than mixes with CDW_MX in which both slag and sodium sulphate were combined.

6 Discussion and interpretation

6.1 Hardening test vs calorimetry for CDW_MX

Figure 6.1 to Figure 6.6 present, the relation between the final normalized heat measured in the TAM Air and the needle penetration depth directly after the calorimetry test was finalized for the samples with CDW_MX and biopolymers.

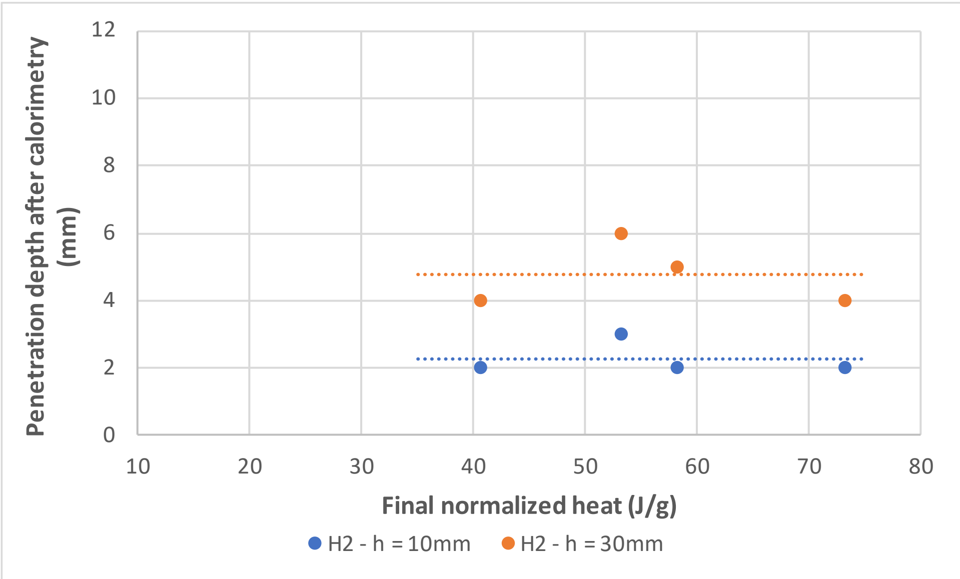


Figure 6.1 Samples with biopolymer H2, Relation final normalized heat vs. penetration depth after calorimetry. A horizontal line with the average value of each set of measurements is shown indicating that the penetration depth and the final normalized heat are independent.

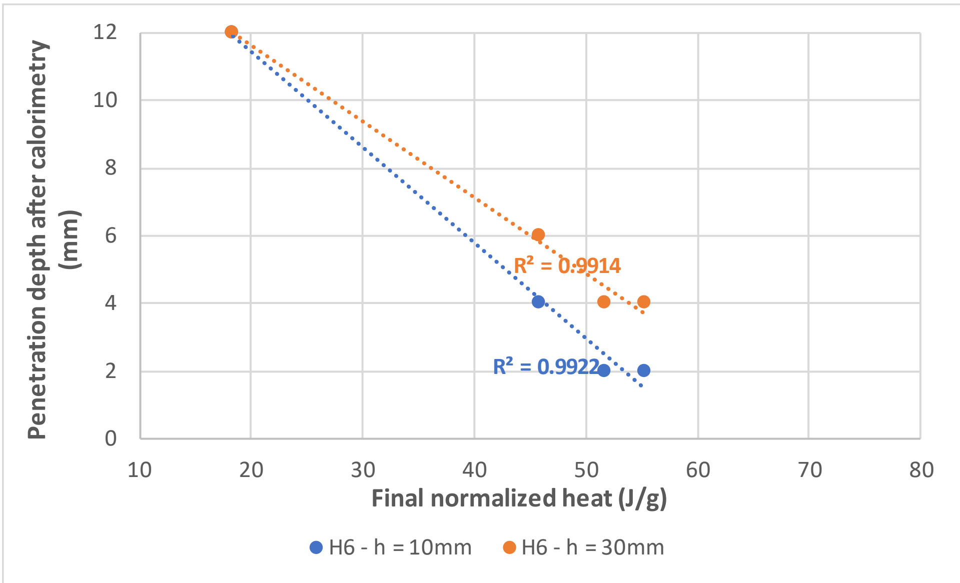


Figure 6.2 Samples with biopolymer H6, Relation final normalized heat vs. penetration depth after calorimetry.

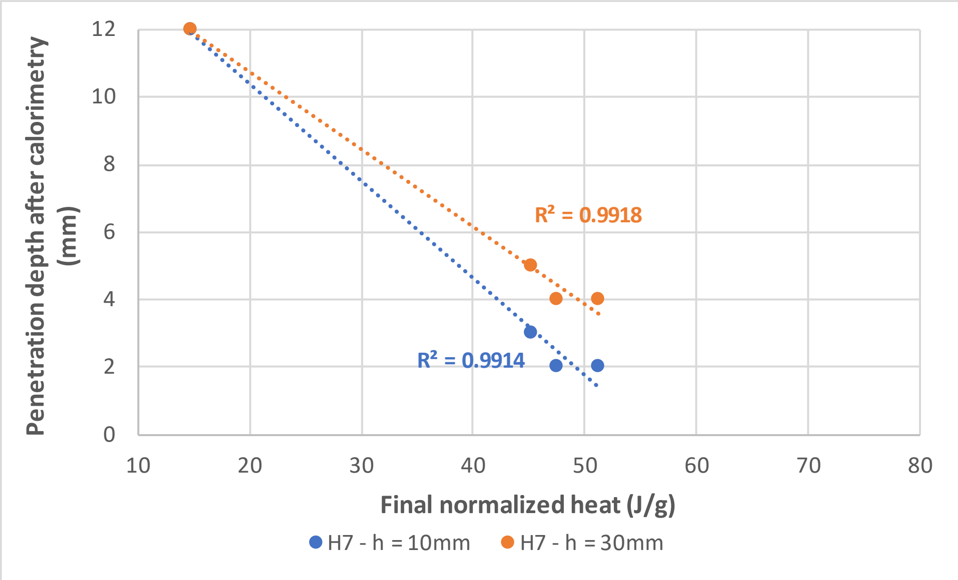


Figure 6.3 Samples with biopolymer H7, Relation final normalized heat vs. penetration depth after calorimetry.

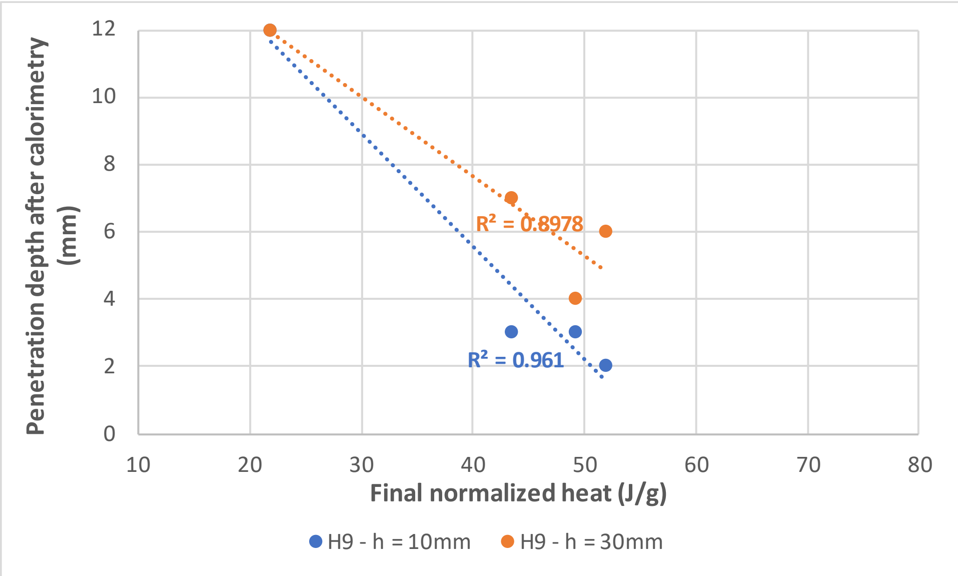


Figure 6.4 Samples with biopolymer H9, Relation final normalized heat vs. penetration depth after calorimetry.

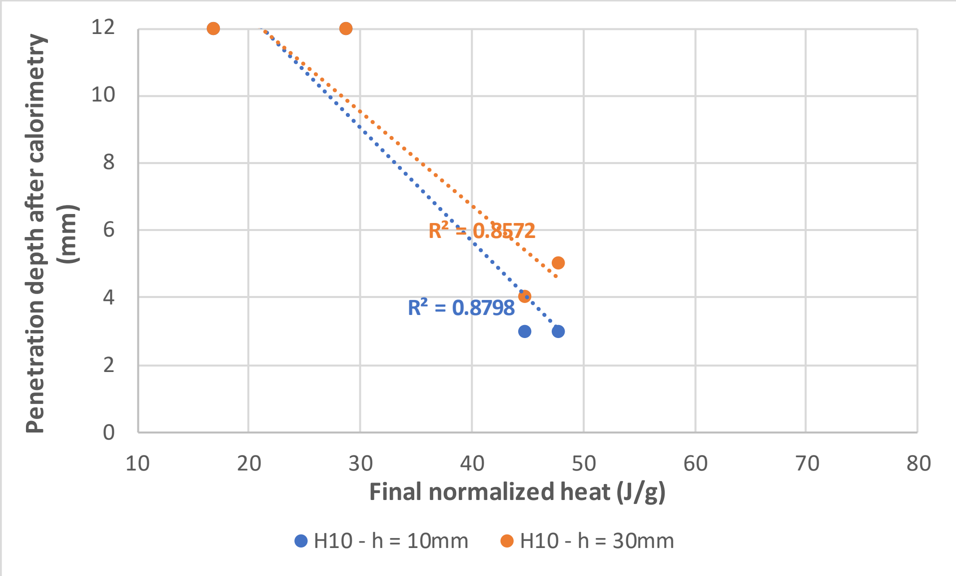


Figure 6.5 Samples with biopolymer H10, Relation final normalized heat vs. penetration depth after calorimetry.

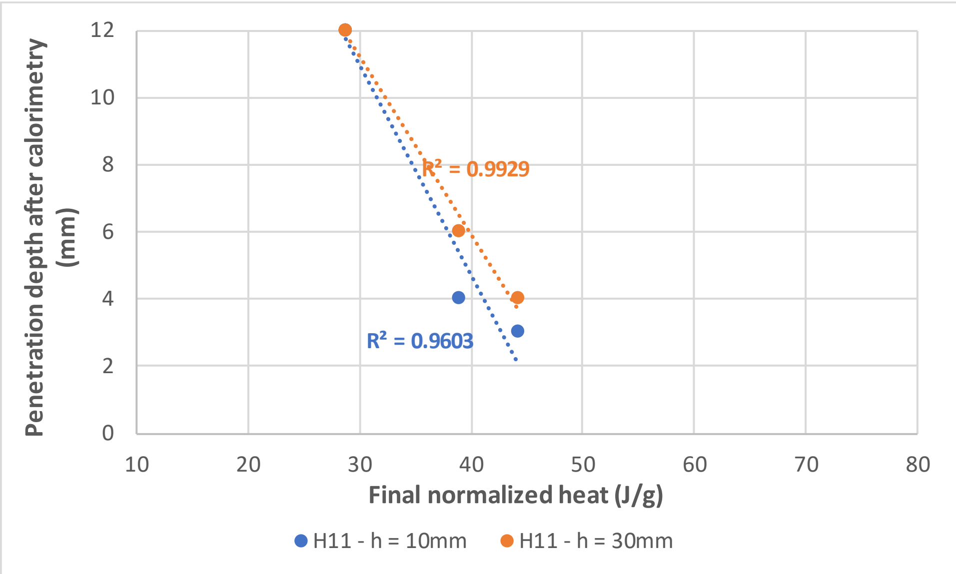


Figure 6.6 Samples with biopolymer H11, Relation final normalized heat vs. penetration depth after calorimetry.

The results indicate that for all biopolymers except for the H2, there is a strong correlation between the final normalized heat and needle penetration. For the H2 mixes, despite of each mix having different heat values, the Vicat test results present very similar penetration depths. This suggests that once the mixes reach certain heat values, the force imparted by the needle at a height of 30 mm is insufficient to differentiate between the hardening levels of the mixes. This can be overcome by increasing the drop height of the needle, as this would increase the kinetic energy of the system and broaden the range of penetration.
An explanation for higher heat values in the H2 mixes is as follows. Based on Figure 6.7 and Table 6.1, it is observed that mixes with biopolymer H9 (ampoules 5 to 8) show a thin layer of water on top of the hydrated phase. In contrast, the amount of water is much less in mix 1

with biopolymer H2 whilst there is no excess water on top of mix 2 to 4. Bleeding of water means that there will be less water available to form hydration products, which in turn means that less heat will be developed. In case of the mixes with biopolymer H2, more water stays in the sample, allowing for a higher amount of hydration products resulting in a lower needle penetration.

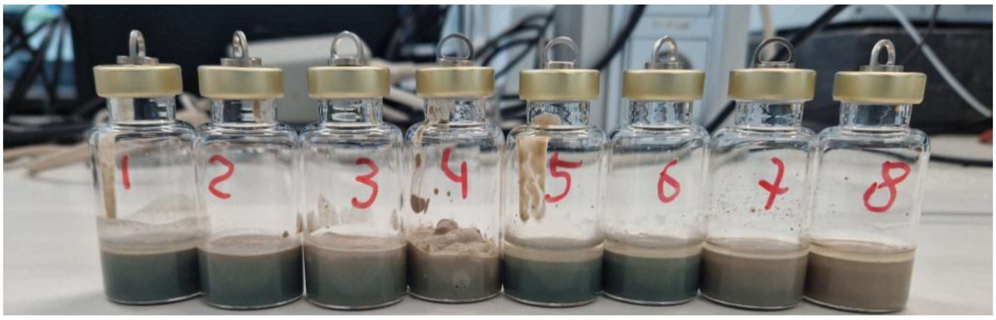


Figure 6.7 Ampoules after calorimetry test with biopolymers H2 (1 to 4) and H9 (5 to 8).

Table 6.1: Composition of ampoules Figure 6.7

Ampoule	Mix
1	80% CDW_MX + 20% GGBS + 4% Na_2SO_4 + 0.1% H2
2	80% CDW_MX + 20% GGBS + 4% Na_2SO_4 + 0.25% H2
3	80% CDW_MX + 20% GGBS + 4% Na_2SO_4 + 0.5% H2
4	80% CDW_MX + 20% GGBS + 4% Na_2SO_4 + 1.0% H2
5	80% CDW_MX + 20% GGBS + 4% Na_2SO_4 + 0.1% H9
6	80% CDW_MX + 20% GGBS + 4% Na_2SO_4 + 0.25% H9
7	80% CDW_MX + 20% GGBS + 4% Na_2SO_4 + 0.5% H9
8	80% CDW_MX + 20% GGBS + 4% Na_2SO_4 + 1.0% H9

6.2 Hardening test comparison between CDW_MX and CDW_SLP

Figure 6.8 to Figure 6.10 present a comparison of the hardening between CDW_MX and CDW_SLP at the same age and for the same Na_2SO_4 content. Note that the samples with CDW_MX have a thickness of 12 mm and the samples with CDW_SLP a thickness of 11 mm.

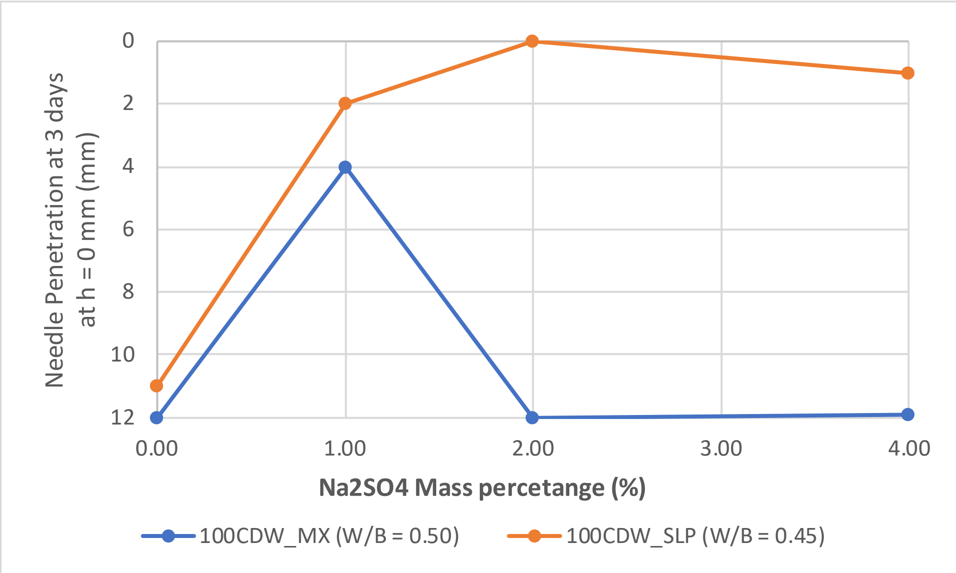


Figure 6.8 Needle penetration comparison between 100CDW_MX vs. 100CDW_SLP for needle drop height h = 0 mm; lines added for the ease of reading only.

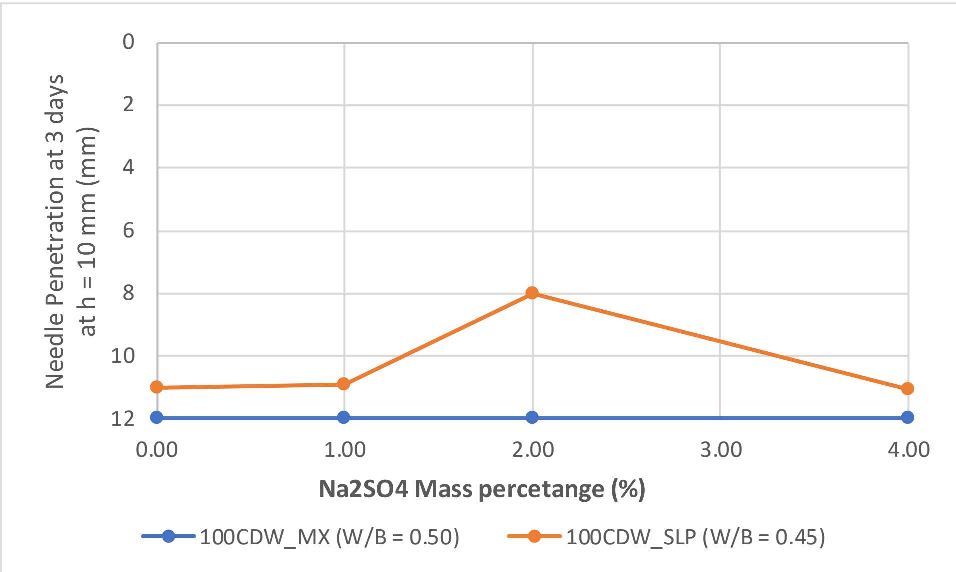


Figure 6.9 Needle penetration comparison between 100 CDW_MX vs. 100 CDW_SLP for needle drop height h = 10 mm; lines added for the ease of reading only.

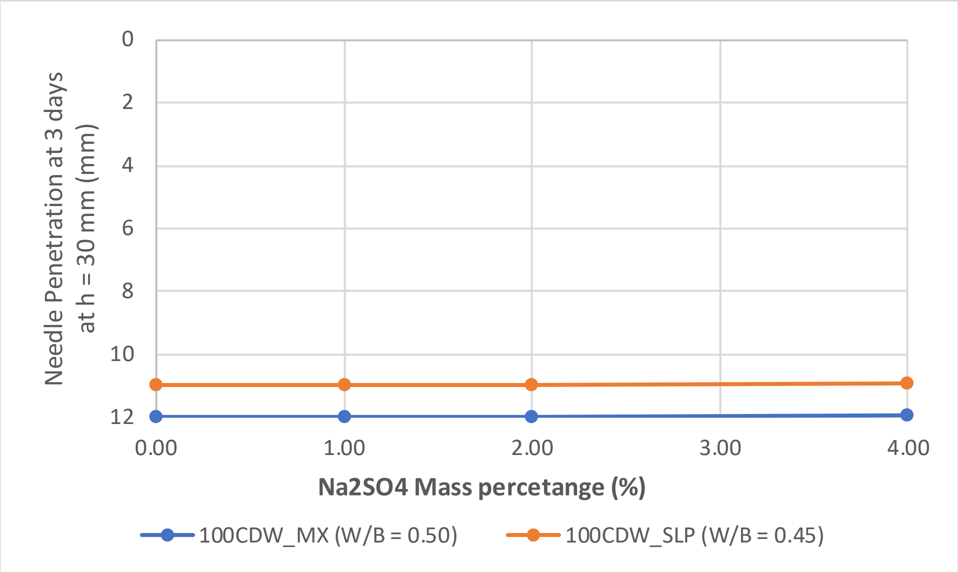


Figure 6.10 Needle penetration comparison between 100 CDW_MX vs. 100 CDW_SLP for needle drop height h = 3 0mm.

The results show that for a needle drop height of 0 and 10 mm, CDW_SLP performs better than CDW_MX, while for a drop height of 30 mm neither of them has a good performance. CDW_SLP potentially develops better binding properties than CDW_MX. Based on the hardening test and mechanical properties of the mortar bars, CDW (regardless of its source) with GGBS and Na_2SO_4 performs better than CDW with either GGBS or Na_2SO_4.

6.3 Mechanical properties vs calorimetry for CDW_MX

Figure 6.11 and Figure 6.12 show the relation between the normalized heat after 65 hours in the Vicat test on binder paste with a high w/b ratio and the bending and compressive strength on mortar bars at 34 days, respectively. The normalized heat and the mechanical properties do not show any relationship. Though calorimetry and the quick scan hardening test show that the mixes with biopolymers produce more heat and have a lower needle penetration, it is not possible to correlate the results of these tests with the mechanical properties.

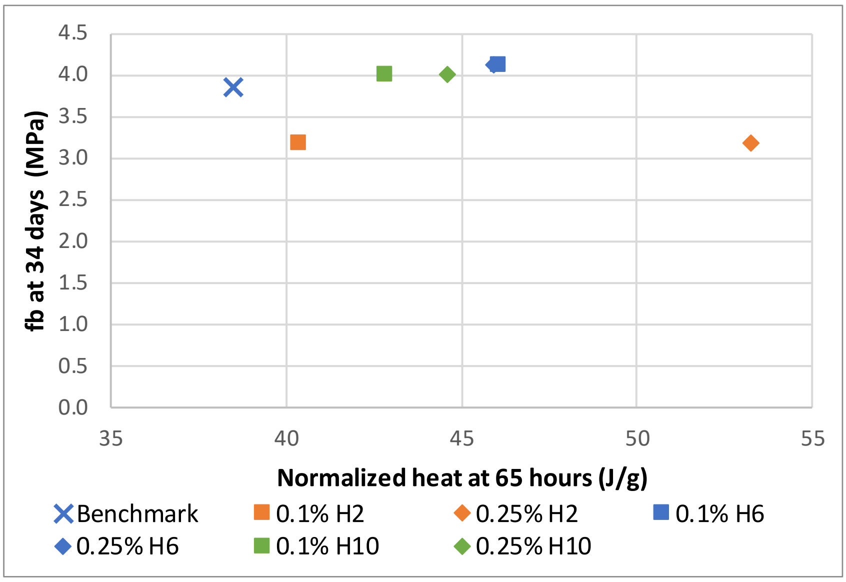


Figure 6.11 Relation between normalized heat at 65 hours and bending strength at 34 days.

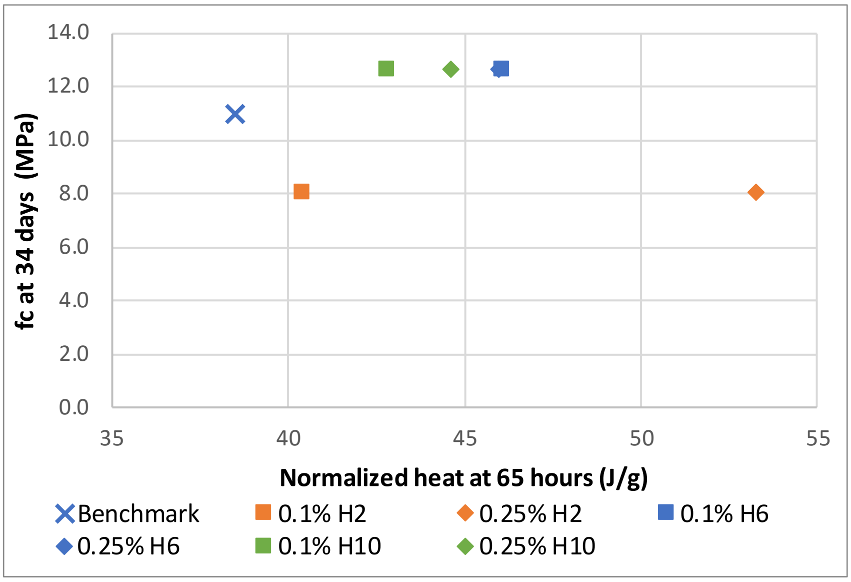


Figure 6.12 Relation between normalized heat at 65 hours and compressive strength at 34 days.

6.4 CDW_MX: Mortar mix design vs. mechanical properties of the mortar bars

Figure 6.13 and Figure 6.14 show the w/b ratio and the bending and compressive strength, respectively, at 34 days of the mortar mixes with 80 % CDW_MX, 20 % slag and 4 % of Na_2SO_4 (see Table 2.11) and for different biopolymers.

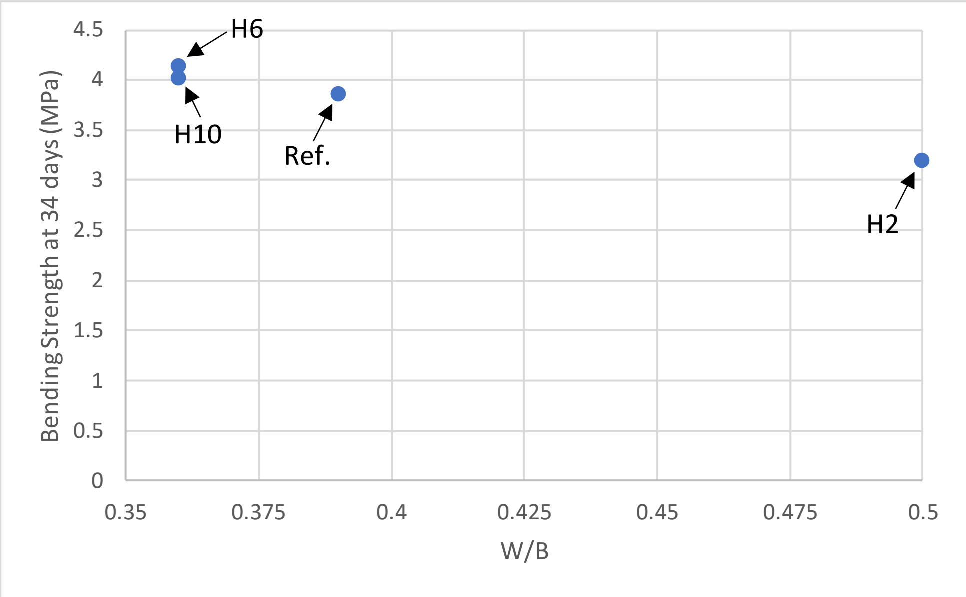


Figure 6.13 Relation between the W/B and the bending strength at 34 days.

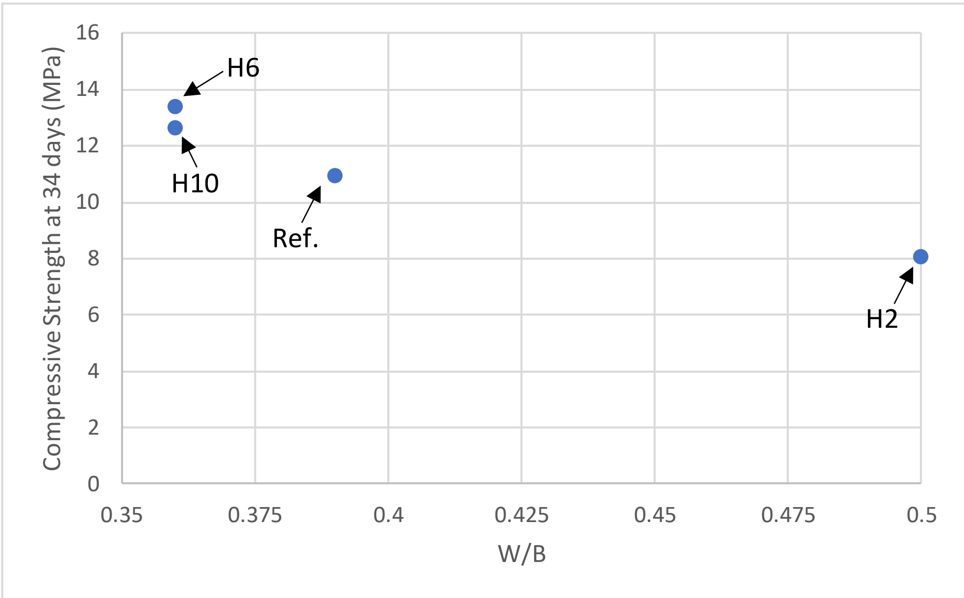


Figure 6.14 Relation between the W/B and the compressive strength at 34 days.

The bending and compressive strength apparently correlate with the w/b of the mixes. However, this does not take into account that the mixes contain different biopolymers, making it questionable if they may be compared. Water demand tests showed that biopolymers H6 and H10 have a plasticizing effect in the mixes. Therefore, these needed less water to reach the same consistency as the benchmark while the mix with biopolymer H2 required a significantly higher amount of water. Generally, there is an inverse relation between the water content of a mix and the mechanical properties. The difference in the strength is likely to be attributed primarily to the water content of the mixes and perhaps to some extent to the effect of the biopolymers in activation of the CDW_MX.

The mixes with CDW_SLP all have the same w/b ratio. The difference in strength can therefore only be attributed to the fact that CDW_SLP with or without Na_2SO_4 is not reactive enough to develop sufficient mechanical properties as also shown by the hardening test. The mix with GGBS develops higher but still low mechanical properties. In the future, CDW_SLP should be combined with both GGBS and Na_2SO_4.

7 Conclusions

- The tests show that neither CDW_MX nor CDW_SLP have sufficient reactivity to develop binding properties on their own. The addition of GGBS and use of Na_2SO_4 is needed to enhance the develop of sufficient mechanical properties.
- In the case of CDW_MX, mixes with GGBS, Na_2SO_4 and additional biopolymers have been evaluated. At paste level, the use of GGBS and Na_2SO_4 together, even at a low percentage (e.g. 90 CDW_MX + 10 GGBS + 1% Na_2SO_4), considerably increased hardening and heat development. The use of biopolymers caused only a slight increment in the heat development of the mixes compared to the benchmark. Mortar mixes with biopolymers H6 and H10, that work as plasticizers, show higher mechanical properties since they had a lower water demand than the reference mix. It is possible that the biopolymers also contribute to the final strength of the mortars by improving the binding capacity of the paste but this could not be substantiated.
- CDW_SLP was tested at paste level with Na_2SO_4, $CaSO_4$, NaOH and biopolymers. The mixes with only Na_2SO_4 performed best, while the mixes with NaOH and biopolymers did not develop any binding properties after 9 days and were discarded. Mortar bars indicated that the use of only GGBS had a better result than the use of only Na_2SO_4. For the future, mixes with both components should be tested, as it was done for CDW_MX.

8 References

[1] J. Visser, J. F. Garzón Amórtegui, S. Hermanns, I. Haaksman, N. Engelen, T. Slaghek, R. Gosselink, V. Wiktor, Cement recycling with help of biobased D1.2 Characterization of two types of ultrafine Construction and Demolition Waste Concrete, TNO R12801, Delft (2022).

[2] I. Haaksman, T. Slaghek, Deliverable report D1.1: characterization of modified carbohydrates and WP 2 materials syneresis, Wageningen University Research, R 2398, DOI 10.18174/5889942 (2023).

[3] V.P. Chakka, T. Zhou, International Journal of Biological Macromolecules Carboxymethylation of polysaccharides : Synthesis and bioactivities, Int. J. Biol. Macromol. 165 (2020) 2425–2431. https://doi.org/10.1016/j.ijbiomac.2020.10.178.

[4] N.L. Vanier, S.L.M. El Halal, A.R.G. Dias, R.E. da Zavareze, Molecular structure, functionality and applications of oxidized starches: A review, J. Foodchem 221 (2017) 1546–1559.

[5] NEN-EN 196-1: Methods of testing cement - Part 1: Determination of strength, (2016).

9 Signature

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