The effect on the hydration process in cement mixed with waste ashes

- A study on three different ashes

Bachelor Thesis in Chemical Engineering

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Abstract

Fly ash have long been used in cement and the effects of it are reasonably well known. Coal fly ash is primarily used and it has many economical and enviromental benefits. There are however other sources of ash that comes from burning other types of fuel. To find a use of these ashes in cement would be of great value. In this study three different ashes are investigated and their effect on the hydration process in the cement. Two of them comes from the burning of waste and one from the paper-industry from burning bark and journal paper.

The ash and cement mixtures were investigated with Vicat, isothermal calorimetry, FT-IR and compression test. The ashes were tested with cement, were the ash content was 10%, 30% and 50% of the total mass. The w/c ratio were set to 0,4 but had to be modified depending on the workability of the mixture. Some ashes also required washing.

Each ash effected the mixture in a different way. The ash with a high unburnt carbon content produced the best strength development. The waste fly ash showed a similar strength development, low energy release and no effect on the setting time. The unwashed cyclone ash had a swelling effect on the cement paste and a poor strength development, but this was negated by washing it. The washed cyclone ash showed an interesting second energy release.

Keywords: Ash, Cement, Hydration, Calorimetry, FT-IR, Vicat, Strength development

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1. Introduction

Most of us have at one point or another come into contact with cement. In our present time, cement has become a fundamental part of the building material we know as concrete, which is cement mixed with aggregrates and water. Without it, the achievements in many fields of engineering, architecture and any fields that make use of it, would have been much harder to accomplish. The environmental effect regarding the large release of carbon dioxide into the atmosphere is perhaps a less well known fact to the public concerning the production and usage of cement. A way to decrease the amount of cement used is to partially substitute it with fly ash. This causes the characteristics of the cement to change, preferably to the better. These effects have been studied and are reasonably well understood but it is desirable to make use of other unused waste ashes [1].

Since the middle of the nineteenth century, Portland cement or Ordinary Portland Cement (OPC), has become the most used cement. Even if it is now not of the same composition, and do not have the same hydraulic activity as when first discovered, it still has the same name associated with it. In concrete the OPC acts as the binder between the aggregates such as sand, stone or any other coarse gravel which are added to give the concrete a certain desired property and durability [2]. Another important ingredient that may be mixed into the cement to increase the strength of the concrete and reduce the heat released during the hydration is fly ash. The fly ashes that are used comes from power plants that burns pulverized coal. To make use of the left-over ash is beneficial since it reduces cost when less cement is needed and it also strengthens the concrete over time [3]. Beside these economical gains there is the environmental approach as the production of cement is a energy consuming process and releases large amounts of carbon dioxide from the burning of limestone. There are however many sorts of fly ashes due to the different types of power plants that make use of different sources of fuel. The effect of these fly ashes when mixed with cement have to be examined.

The hydration of OPC and the added ingredients are difficult to understand due to the complex and different mechanisms involved. This needs to be examined further because it gives practical advantages in determining which species of waste ash that increase the concretes performance [4].

2. Aim

This report will investigate the effects on the early hydration process that occurs when Portland cement is mixed with ash from different sources. Three different ashes are applied: one with a high level of unburnt carbon, one cyclone ash with high amounts of sand and metal and one fly ash. The latter two comes from the burning of waste.

3. Theory

3.1 Notations

The chemical composition of OPC consists mainly of four mineral phases [5]:

Alite	Ca_3SiO_5	(50-70 mass%)
Belite	Ca_2SiO_4	(15-30 mass%)
Aluminate	$Ca_3Al_2O_6$	(5-10 mass%)
Ferrite	$Ca_4Al_2Fe_2O_{10}$	(5-15 mass%)

In cement chemistry different shorthand are used for the different mineral compositions and those are not to be read as the structure of mineral but only as a easier way to write it [2][5].

$C = CaO$ $A = Al_2O_3$ $S = SiO_2$ $\acute{S} = SO_3$

$F = Fe_2O_3$ $H = H_2O$ $f = FeO$ $M = MgO$

The chemical compositions above are then written as follows:

Alite = C_3S

Belite = C_2S

Aluminate = C_3A

Ferrite = C_4AF

OPC are however not pure in the sense that it only contains the above mentioned minerals but also ions such as Fe^{3+}, Mg^{2+}, Al^{3+}, Si^{4+}, Na^+ and K^+. These ions are not written out since the mineral names show the structures that are more important to the chemistry of cement.

3.2 Production of OPC

When manufacturing Portland cement clinker, different raw materials are used. In certain proportions limestone, chalk, clay, sand and other components are mixed. Limestone and chalk are used to provide the important mineral CaO while the addition of different clays and sands is to provide Al_2O_3, Fe_2O_3 and SiO_2 [6]. The materials are first dried or wetted depending on the homogenization in the mixture with a following step of grinding. After this the mixture is run through a kiln where the temperature of the materials are heated up to 1350-1450 °C in order to form the desired clinker phase. It ends with cooling the material and a follow up grinding of the clinker into a fine powder, during which $CaSO_4 \cdot 2H_2O$ (gypsum) is added. This heating and cooling process can be described as follows [6]:

Temperature range 20-1250 °C:

- Water escapes and the clay decomposes and dehydrates
- Dissociation of $CaCO_3$ into CO_2 and CaO and the formation of C_2S
- Binding of the activated minerals provided by the clay and sand with C_2S
- A melt is formed of C_2S

Temperature range 1250-1450 °C:

- In the activated melt C_3S is formed as C_2S and CaO combines

Cooling:

- Formation of C_3A and C_4AF and the slower the cooling will result in a larger formation of these minerals

3.3 Hydration process and resulting products of OPC

OPC is a hydraulic cement meaning that it reacts with the presence of water, ranging from moisture to liquid, by forming a paste that ends in a hardening. The chemical term is described as an: anhydrous compound that forms a hydrate when it comes into contact with water [2]. The amount of water that is needed depends on the fineness of the cement and added materials so that a higher degree of fineness of the particles demands a higher water/cement (w/c) ratio. This is because the hydration process takes place between the cement particles and in the water that surrounds them as soon as cement is added in water [6]. When cement and/or cement mixture is mixed with water it undergoes three stages, the first being fresh cement paste without any strength. In the second stage the paste losses plasticity and is called setting. The third and final stage is called hardening that gives the cement strength and hardness [2].

3.4 Reaction products of OPC

The largest component of OPC is C_3S. It is the important component that reacts to give cement its strength when it hydrates into calcium silicate hydrates (C-S-H) and calcium hydroxides according to the following reaction [2]:

$$3CaO\cdot SiO_2 + (3+m-n)H_2O \rightarrow nCaO\cdot SiO_2\cdot mH_2O + (3-n)Ca(OH)_2 \quad (3.4.1)$$

Because calcium silicate hydrate is amorphous and varies with a wide range of configurations and compositions, the terms C-S-H phase or just C-S-H are used. The amount of calcium hydroxide needs to be kept at a high level to have a high pH level that protects the iron from oxidation in reinforced concrete:

$$Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O \qquad (3.4.2)$$

By keeping the amount of calcium hydroxide high, the calcium hydroxide near the surface reacts first and thus keep a high pH level near the iron deeper inside the concrete. Other components, besides the clinker, can form similar hydration products as clinker would form by reacting with calcium hydroxide. If too much of these pozzolanic materials are added with the cement the risk are that the level of calcium hydroxide becomes too low and will therefore be insufficient to protect against oxidation of the iron bars [6].

This first reaction starts immediately when cement is mixed with water, and stops after a few minutes and starts again after the dormant period is over after a couple of hours. These reactions gives the cement its early build up of strength during the first 28 days. C_2S do not react as fast and do not give as much strength as C_3S during the first 28 days but over a longer time period of a year it give as much strength as C_3S [1][6].

C_3A are important to have in the production of cement clinker because during the melt it helps the formation of C_3S and C_2S. In the finished product it can react to quickly with water and cause the setting of cement to occur to quickly. Sulfates, existing in the gypsum, prevent this by reacting with the dissolved aluminate. It is known that when clinker is ground down into a powder with no gypsum being added, the addition of water causes an almost immediate setting. A addition of a specified amount of calcium sulfates, depending on the sought after characteristics of the cement, prevents this quick setting and allow the dormant period to occur [6]. C_4AF, the mineral that gives cement the well known grey colour shares similar reactions with C_3A. Initially it reacts quickly to slow down when the hardening process begins [5].

3.5 Fly ashes

The classification of fly ashes falls under three different categories [2][3]:

Class F: Contains a low content of CaO from burning anthracite or bitumenous coals. They have pozzolanic properties but rarely harden by themselves. The crystalline contents usually are hematite, magnetite, mullite and quarz.

Class C: The CaO content is higher in these fly ashes resulting from the burning of lignite or sub-bituminous coal. These ashes are pozzolanic and can act as cement on they own. A highly reactive component of Class C ashes are calcium alumino-silica glass and the crystalline minerals includes anhydrite, C_3A, C_2S, C_4A_3S, gehlenite, hematite, lime, mullite and quarz.

Class N: This class contains raw or calcined natural pozzolans. This class contains volcanic ash, shale, calcined kaolin clay and other similar substances.

When fly ashes are mixed with OPC, the free calcium hydroxide slowly reacts with the calcium alumino-silicates during the hydration. This produces more cementious products described below with a simplified (3.4.1) [3]:

OPC reaction: $C_3S+H_2O \rightarrow C\text{-}S\text{-}H+Ca(OH)_2$ (3.4.1)

Pozzolanic reaction: $Ca(OH)_2 + SiO_2 \rightarrow C\text{-}S\text{-}H$ (3.5.1)

The amount of fly ash affects the water demand. A fly ash content between 15-20 % demands less water and a content above 20 % demands more water, in order to keep a constant workability of the ash. This increase the plasticity of the paste because fly ashes have a glassy surface and a finer particle size than the cement which it replaces. Ashes with a large amount of unburnt carbon, meaning a loss of ignition (LOI) is greater than 1 %, increase the water demand in order to have a good plasticity [3].

3.6 Infrared spectroscopy

All molecules vibrates and when a photon strikes a molecule it can raise the energy of that molecule causing it to vibrate in a different way. This means that the molecule has entered a more excited state when it absorbed the energy of the photon [7]. This is mainly caused by light in the infrared spectrum. By striking a sample with infrared radiation and measuring the amount of photons that the sample absorbs, it can be determined what molecules that are present in that sample [8]. The reason for this is that molecules absorb photons at certain frequencies, mostly different, but may in some cases be identical [5].

The energy of a photon that is emitted is given by:

$$E=h*v \qquad (3.6.1)$$

E is the energy, h is the Planck constant ($6,626 *10^{-34}$ J s) and v is the frequency. The different energy levels between E_0 and E_1 can thus be written as [9]:

$$\Delta E=h*v \qquad (3.6.2)$$

Electromagnetic radiation is described in the following equation:

$$c=\lambda * v \qquad (3.6.3)$$

c is the light velocity in vacuum (2,997925 * 10^8 m s^{-1}), λ is the length between adjacent peaks and v is the frequency.

In infrared spectroscopy the wavenumber, $\tilde{v}$ which is cm^{-1}, is widely used and the relationship between $\tilde{v}$, λ, v and c is given as follows:

$$\tilde{v}=1/\lambda=v/c \qquad (3.6.4)$$

Combining equations (3.6.2), (3.6.3) and (3.6.4) the following equation is received and it shows the absorption of radiation in wavenumber:

$$\tilde{v}=(\Delta E*c)/h \qquad (3.6.5)$$

A molecule that has energy vibrates because of that. These vibrations are observed between 600 - 4000 cm^{-1} also known as normal fundamental frequencies when stretching and deformation occurs and are used for identification and characterization [9]. A molecule can vibrate in any direction in space in the coordinates X, Y and Z. The degree of freedom a polyatomic molecule is of the maximum of $3N$ where N is the number of atoms in the molecule. There are limitations when it comes to vibrational modes depending on the molecule structure depending on if the structure is non-linear or linear. Water, with the hydrogen atoms pointing up from the oxygen, is a non-linear molecule that makes the degree of freedom become $3N - 6$. CO_2, with the oxygen atoms on either side of the carbon atom, is a linear molecule and the degree of freedom become $3N - 5$.

Stiffness on the bond between and masses of the atoms at the end of each bond also explains the vibrational modes. The proportionality constant, the force constant k which is derived from Hooke's law, can be used to characterise the stiffness of the bond between atoms. To simplify calculations is to combine them in a way called reduced mass denoted μ. m_1 and m_2 signifies the mass of the atoms at the ends of a bond [8]:

$$\mu=m_1m_2/(m_1+m_2) \qquad (3.6.7)$$

With the involvment of the force constant the frequency of absorption becomes:

$$v = (1/2\pi)*(k/\mu)^{1/2} \qquad (3.6.8)$$

The modify equation (3.6.8) into wavenumbers the equation then becomes as follows:

$$\tilde{v} = (1/2\pi c)*(k/\mu)^{1/2} \qquad (3.6.9)$$

The $v_{1\text{-}4}$, denotes which vibrational mode a molecule has, as can seen in Table 4, and shows in what way the molecule vibrates when the light in the spectrometer agitates it. Water, a polyatomic molecule, may vibrate in three different modes, namely v_1, v_2 and v_3. v_1 means that the hydrogen atoms stretches away from and back towards the oxygen atom symmetrically. v_2 means that the hydrogen atoms bends away from each other, in the manor like the blades of a scissor open and closes. v_3 is similar as v_1 with the difference that the hydrogen atoms stretches asymmetrically, one moves away while the other move toward the oxygen atom. v_4 for CO_3 is an out-of-plane bending of the molecules described best as stretching the top of a pyramid from its base [5][7][10].

4. Materials

4.1 Equipment

Matest Vicatronic Model E044N, as seen in Figure 1, were used to measure the setting time of the cement mixtures and will be referred to as Vicat in this report [11].

Figure 1: The Vicatronic machine used to measure setting time and picture was taken during a test.

ELE International Model 39-0031 is an automatic/manual mortar blender. It was used to blend the mixtures for the Vicat measurements. The mixing head operated at 62 rpm and the mixing blade at 140 rpm.

Isothermal calorimetry will be referred to as calorimetry in this report, was measured using a device specially built for this purpose. The device consists of a heat sink, a heat-flow sensor, sample holders for the samples and a reference and is isolated to keep a constant temperature, see Figure 2[*] [5]. The temperature inside was kept at a constant with a thermostat which were controlled by a thermoelectric air-air heater cooler (AA-100-24-22, SuperCool, Gothenburg,

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[*] With consent from its original maker, Rikard Ylmén, this picture was drawn with the original as a model.

Sweden). By keeping the temperature at a constant the heat release inside the cement could be measured and plotted.

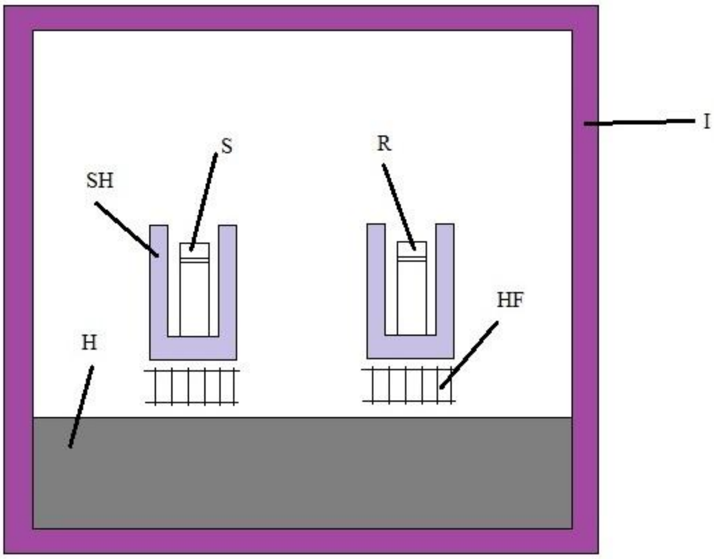

Figure 2: Schematic on the isothermal caliometer used in this paper. Heat sink (H), heat-flow sensor (HF), isolated container (I), reference (R), sample (S) and sample holder (SH).

A spectrometer, Thermo Scientific Model Nicolet 6700 FT-IR, Figure 3, was used to measure the absorbance spectrum and will be referred to as IR in this report [12].

Figure 3: The spectrometer being used for the spectroscopic measurements.

A force blender called UEZ Mischtechnic with the difference being that the one used at CBI had three mixing arms [13]. Compression was carried out at CBI, located at KTH in Stockholm. The machine, from the company MTS, model MTS 4500 kN, compresses a concrete cube to measure the pressure strength. A cube are placed between the pistons, see Figure 4, which were then compressed until the cube breaks according to the standard SS-EN 12390-3.

Figure 4: Image of the MTS machine showing the parts that measured compression strength.

4.2 Cement

The cement used in this report was a Portland limestone cement from Cementa AB with the product name “Byggcement CEM II/A-LL 42,5 R” [5].

4.3 Ashes

Further down an ash is mentioned as washed or unwashed. The meaning of this is that when an ash is taken out from the system it may be mixed with water. A washed ash has been mixed with water and an unwashed ash has not been mixed with water.

Municipal Solid Waste Fluidized Bed Combustion Cyclone ash or MSW FBC Cyclone ash is an unwashed ash and will be referred to as cyclone ash in this paper.

Municipal Solid Waste Grate Fired Boiler Fly ash or MSW GFB Fly ash is a washed ash and will be referred to as fly ash in this paper.

The paper/wood ash will be called wood ash in this paper and comes from the burning of bark and old journal paper. Contents are given in Appendix, Table 6.

4.4 Other materials

Aggregates are additives in concrete to lessen the amount of cement being used. Aggregates used at CBI were gravel with the radius ranging between 0-8 mm, and small stones with the radius between 8-16 mm. Aggregates were only used during the tests conducted with the MTS machine. An admixture known as a plasticiser, ACE Glenium 51 from the company BASF, were used during the test conducted with the MTS to increase the plasticisty of the cement since the amount of water was insufficient to make it workable. Limestone powder, in this case Limus 25 was used, but only during the casting for the compression tests [14]. The use of limestone powder is mainly adopted in France and Sweden. Mixed with concrete it enhance the hydration of cement and increase the strength development [15].

5. Experimental

5.1 Equations

The ratio of water, or w/c ratio, is generally used to define the amount of water that are to be added to the cement or cement mixture. In these experiments the ratio r of 0,4 was set as a standard. The w/c ratio is calculated as follows [2]:

$$r=w/c \qquad (5.1.1)$$

The w defines the mass of water that was used and c stands for the mass of dry cement mixture that was used.

To be able to calculate the energy release during the caliometric experiments it was required to convert the millivolts U obtained from the machine into milliwatts P. This was performed with each data point given. There were two constants, k_1 and k_2, one for each sample holder which had been experimentally calculated and were specific for the isothermal calorimetry apparatus. First calculate the product of k_1 or k_2 multiplied with U. Divide that result with the mass m of added dry cement mixture. The value recivied shows energy per gram concrete and the equation looks as follows:

$$P=(k*U)/m \qquad (5.1.2)$$

$k = k_1$ or k_2 = constant for sample holder; $k_1 = 6{,}986$ and $k_2 = 7{,}239$

The spectrometer collected data every 10 minutes in order to measure the absorbption of the sample at that specific time $a_{(t)}$. The plotted results makes it possible to visually see the change over time. To visualise growth or decay of a substance in a sample at certain time intervals and at corresponding wavelengths, the first measured absorbance spectrum $a_{(t1)}$ was subtracted from the absorbance spectrum at a desired time interval $a_{(t2)}$, and the equation therefore looks like this:

$$a_{(t)}=a_{(t2)}-a_{(t1)} \qquad (5.1.3)$$

$a_{(t)}$ = absorbance difference at time t

$a_{(t2)}$ = absorbance at time $t2$

$a_{(t1)}$ = absorbance at time $t1$

5.2 Vicat

A total of 10 different mixtures were tested with the Vicat machine. A sample of 100 mass% OPC was the standard sample the 9 other mixtures was compared with. All samples were mixed with distilled water. Three different fly ashes: cyclone ash, wood ash and fly ash were tested with three different percentage amounts of the total dry mixture mass of 300 grams, which were 10 mass%, 30 mass% and 50 mass%.

5.2.1 Preparation of materials for Vicat measurements

Some ashes caused problems regarding the workability of the paste that made it necessary to adjust the amount of water added. A strict adherence to equation (5.1.1) was therefore abandoned in order to get a acceptably workable cement paste to fill the mould. This problem have been studied [3].

The blending procedure was made by first blending and mixing the OPC and ashes by manually shake and rotate the cup containing the mixture for 3 minutes. The exemption here was the cyclone ash and moist fly ash. If an ash sample already contained water it would start the reaction early if it was mixed with cement.

The cyclone ash did not show any problems with the w/c ratio but during the measurement in the Vicat the paste started to swell, which will be discussed in chapter 6.1. Therefore the first cyclone ash test of 10 mass% was added in 120 grams of water and left for 20 hours in the blender bowl before a test was conducted. The 30 mass% and 50 mass% test amounts were added in 200 grams of water in plastic bottles for a period of 6 and 7 days respectively. This large amount of water was applied to avoid any setting or hardening of the ash before it was used in any tests. Before each test 50 grams of water was removed which was easily made possible since the cyclone ash had formed a sediment on the bottom. The w/c ratio was chosen to be 0,5 in order to increase the workability of the paste.

The fly ash already had some water bound to it from the washing process. Because of the w/c ratio was set to 0,4 the amount of water in the ash had to be determined. The ash was therefore gently ground to a lose powder which made it easier for the water to evaporate and left to dry for 3 hours. After this time period the ash had lost 14 mass% and left for 22 hours only slightly increased this amount to 15 mass%, so the fly ash was therefore calculated as already containing 15 mass% water. The ash consisted of lumps due to the water so before each blending, the amount in Table 1 was ground down manually in order to achieve such a good homogeneous mixture as possible.

Figure 5: Fly ash, before being manually ground down, show the formation of existing lumps.

The wood ash required some manual grinding to get rid of the existing lumps, similar to fly ash lumps in Figure 5, before being mixed with OPC. The ash did not however contain any water and was already dry. The ash demanded more water when a higher amount of ash was added in the mixture to make the paste workable. Own practical test was made so that the amounts of water needed for each of the 10 mass%, 30 mass% and 50 mass% measurements were 120 grams, 180 grams and 240 grams respectively. Thus the w/c ratio became 0,4, 0,6 and 0,8.

5.2.2 Execution of each sample measurement for Vicat measurements

A sample was prepared by first adding water into the blender bowl, followed by the wet ash and lastly the OPC. If an ash was dry it was already mixed with the OPC so the water was added first and then the dry mixture. The blending was started and run for 2*90 seconds. After the first 90 second period the bowl was removed and the walls was scraped. This was done so that any mixture that had got stuck on the walls was added to the paste being mixed. This took around 20 seconds and then the last 90 seconds of mixing was performed. After this blending procedure the paste was added into the mould that was filled to the brim as seen in Figure 6.

A standard test, EN 196-3:2005, was run which was set to a 16 minutes interval between each of the 26 measurements. The amount of time elapsed from the adding of ingredient into the water and the first measurement was around 10 minutes. The following amounts were mixed in the blender with the numbers rounded off to the closest whole number as shown in Table 1. In Appendix, Figure 44, all measurements are given.

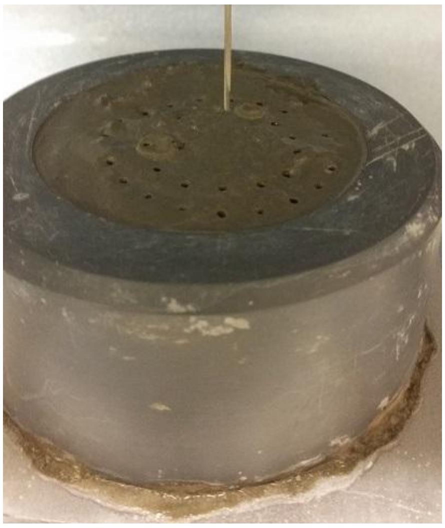

Figure 6: A mould filled to the brim during a Vicat test, in this case pure OPC.

Ingredient	**Masspercentage (%)**	**Ash (g)**	**OPC (g)**	**Dry mass (g)**	**Water (g)**
OPC	100	0	300	300	120
Cyclone ash (washed)	10	30	270	300	120
	30	90	210	300	150
	50	150	150	300	150
Wood ash	10	30	270	300	120
	30	90	210	300	180
	50	150	150	300	240
Fly ash	10	35	270	300	115
	30	105	210	300	105
	50	176	150	300	94

Table 1. Table over amounts of ingredients mixed for the Vicat tests.

5.3 Isothermal calorimetry

A total of 15 test were run with the isothermal calorimetry machine. A sample of 100 mass% pure OPC was to be the standard. Mixtures of OPC with 10 mass%, 30 mass% and 50 mass% of each ash and 3 measurements of 100 mass% pure ash were mixed with distilled water. The three different ashes was cyclone ash, wood ash and fly ash with the above percentage mixtures.

5.3.1 Preparation of materials for calorimetry measurements

To reduce the effects of temperature fluctuations inside the container, see Figure 2, each test sample had an adjacent reference sample that would not create any energy. In these experiments a small plastic container with distilled water was used. The distilled water was allowed to reach equilibrium with the temperature inside before any measurements were performed.

Exception of a w/c ratio of 0,4 was made for wood ash that needed a higher water ratio (discussed above) and the washed cyclone ash that had a w/c ratio of 0,5. This was done because experiments with the washed cyclone ash and Vicat showed that the ratio of 0,4 was just enough for 10 mass% of cyclone ash to have a good workability. The w/c ratio was not expeced to affect the energy release from the mixture in a significant way. Earlier research has shown that the amount of water that is used do not have a large of an impact on the results [5].

The cyclone ash that was washed was put in a small glass cup with 10 grams of water and left for 18 hours. Before the OPC was added with the wet ash excessive water was removed using a plastic pipett in order to attain a w/c ratio of 0,5.

Some of the fly ash were ground manually and left to air dry in a laboratory room for 24 hours and was then considered dry when being weighed for the tests. Otherwise they were weighed as though they contained 15 mass% water. So the amount of water added in Table 2 are shown as the amount needed to reach w/c ratio of 0,4.

Inside the container the temperature was kept at a constant level. The measured data were given in mV which were inserted in (5.1.2) to obtain mW/g.

5.3.2 Execution of each sample measurement for calorimetry measurements

A sample was prepared by first weighing the amount of ingredients needed and a blending of the dry mass constituents as discussed in the experimental part in chapter 5.2. Each sample was to have a total weight of 5 grams of dry mass and 2 grams of water to obtain the desired w/c ratio. The preparation was made by first adding the amount of water into a small plastic container. The dry mass mixtures were then poured into this plastic container and manually mixed with a glass rod for 3 minutes to simulate the blending time in the Vicat tests.

When the glass rod was removed from the mixture a small amount of sample followed the glass rod and the amount lost was estimated to be approximately 0,15 gram. The container was closed and placed to the side whilst another sample was prepared in the same way. When this was done the plastic containers were lowered into the calorimetry machine which was set to take a measurement every 10 seconds. The time it took from the first sample being prepared until measurements began was 10 minute. The amounts that were measured in the machine are shown in Table 2 with the values rounded off to closest number with one decimal. In the case of 100 mass% pure cyclone ash the amount of water needed was 3 gram to get the ash to form a paste (w/c ratio = 0,6).

Ingredient	**Masspercentage dry mass (%)**	**Ash (g)**	**OPC (g)**	**Dry mass (g)**	**Water (g)**
OPC	100	0	5	5	2
Cyclone ash	10	0,5	4,5	5	2
	30	1,5	3,5	5	2
	50	2,5	2,5	5	2
	100	5	0	5	3
Cyclone ash (washed)	30	1,5	3,5	5	2,5
	50	2,5	2,5	5	2,5
Wood ash	10	0,5	4,5	5	4
	30	1,5	3,5	5	4
	50	2,5	2,5	5	4
	100	5	0	5	6
Fly ash	10	0,5	4,5	5	2
	30	1,5	3,5	5	2
	50	2,9	2,5	5	1,6
	100	5,9	0	5	1,1

Table 2: Table over amounts of ingredients mixed for the calorimetric measurements.

5.4 Infrared spectroscopy

A total of 15 measurements were performed using the spectrometer. A pure sample of 100 mass% OPC was the standard and mixtures of OPC with 10 mass%, 30 mass% and 50 mass% of each ash and 3 samples of pure ash. All samples were mixed with distilled water.

5.4.1 Preparation of materials for infrared spectroscopy

The amounts of ingredient that were mixed are given in Table 3. The procedure of washing the cyclone ash was performed in the same way as in isothermal calorimetry and are described in chapter 5.3.1.

The wood ash contained small pieces of unburnt carbon with a diameter of 1-3 mm so when measuring up the different amounts these particles were removed by gently shaking the spoon or cup. The particles would rise to the surface of the ash and could then be removed. The reason for this removal was that the measuring surface was small. If a small piece of carbon was to enter that surface it would occupy a relatively large area and the measurements would thus measure un-reactive carbon.

To avoid a quick evaporation of water from the small amount of paste some steps had to be taken. A small plastic lid, a new for each test, had been cut beforehand to fit under the clamp. The sample was placed under the lid and strips of parafilm were pressed around the lid to prevent evaporation of water as shown in Figure 7.

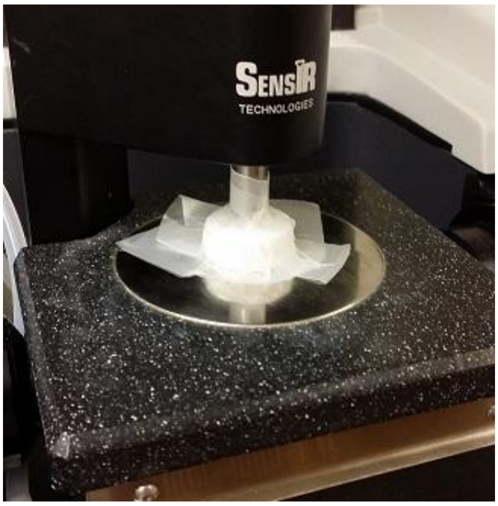

Figure 7: Precautions made to ensure that water was prevented to evaporate.

5.4.2 Execution of each sample measurement for infrared spectroscopy

Each sample was prepared by first measuring the amount of water in a small glass cup. The dry material was then poured into this cup and the manual blending started with a small glass rod. After manually blending the paste for 3 minutes, a sufficient amount of the paste was applied with the glass rod onto the measurement surface of the spectrometer. The clamp was tightened with the small plastic lid attached and the measuring was started. The time elapsed from the pouring of the cement mixture into the water and the manual blending until measurements began was 3 minutes. Reference time for all spectroscopy measurements were 4 minutes, counted from the initial mixing of ingridients. The data obtained was then calculated with equation (5.1.3). Spectroscopy measurement of the standard may be found in Appendix, Figure 43. In order to analyze the data from the measurements done with the spectrometer, Table 4 is consulted [16].

Ingridient	**Masspercentage dry mass (%)**	**Ash (g)**	**OPC (g)**	**Dry mass (g)**	**Water (g)**
OPC	100	0	5	5	2
Cyclone ash	10	0,5	4,5	5	2
	30	1,5	3,5	5	2
	50	2,5	2,5	5	2
	100	100	0	5	2
Cyclone ash (washed)	30	1,5	3,5	5	2,5
	50	2,5	2,5	5	2,5
Wood ash	10	0,5	4,5	5	2
	30	1,5	3,5	5	3
	50	2,5	2,5	5	4
	100	5	0	5	6,5
Fly ash	10	0,5	4,5	5	2
	30	1,8	3,5	5	1,7
	50	2,5	2,5	5	2
	100	5	0	5	2

Table 3. Sample compositions for the infrared spectroscopy measurements.

Wave number (cm^{-1})		**Possible assignment**
656-658		v_4 of SiO_4
714		v_4 of CO_3
847-848		Al-O, Al-OH
877-878		v_2 of CO_3
1011-1080		Polymerized silica
~1100-2200		v_3 of SO_4
1200-1202		Syngenite[*], thenardite[**]
1400-1500		CO_3
1620-1624		v_2 of water in sulphates
1640-1650		v_2 H_2O
1682-1684		v_2 of water in sulphates
1795-1796		$CaCO_3$
2513-2514		$CaCO_3$
2875-2879		$CaCO_3$
2983-2984		$CaCO_3$
3319-3327		Syngenite, thenardite
3398-3408		v_3 of H_2O, capillary water
3457		$v_1 + v_3$ of H_2O
3554		v_3 of H_2O in gypsum
3611		Bassanite[***]
3641		$Ca(OH)_2$

Table 4. Possible assignments for the observed peaks in the spectroscopy measurements.

5.5 Compressive strength measurements

A total of 6 different mixtures were tested with the MTS machine, see Figure 4. The mixtures were made of pure OPC being the standard, unwashed cyclone ash with 30 mass% and 50 mass%, wood ash with 30 mass% and a washed 50 mass%, and fly ash with 30 mass%.

The wood ash that was washed was performed by adding 4 kg of ash in roughly 15 dm^3 of water and allow to sink. The largest coal particles that were floating on the surface or in the water were removed. Calculation was made how much water that had been absorbed by the ash in order determine how much ash and water that was to be mixed in Table 5.

---

[*] $K_2Ca(SO_4)_2\cdot H_2O$

[**] Na_2SO_4

[***] $CaSO_4\cdot 0,5H_2O$

The w/c ratio of 0,45 was calculated on the amount of OPC, Limus 25 and ash, not counting the aggregates as dry mass.

Figure 8: Mould for casting concrete cubes to be used in compression testing. In this case 9 cubes filled with unwashed 30 % wood ash mixture.

The percentage amount of ash in each mixture was balanced by removing Limus 25. Therefore the amount of OPC stays the same in all of the castings and only the amount of Limus 25 changes.

A sample preparation was made by first mixing all the dry components for at least 2 minutes or until the mixture were homogenous. The water was added and the blender was run for 1 minute. Then the lid was opened and material that had stuck to the corners was scraped down so they also got mixed and after that the blender was run for 1 minute. The plasticiser was added and the blender was run for 2 minutes after which the cement mixture was cast in the moulds. The amount of plasticiser added had to be carefully applied to get a good workable concrete as in Figure 36. The difference of plasticity between no plasticiser and too much plasticiser can be seen in Figures 9 and 10.

The samples were cast in cubes with the dimensions 15*15*15 cm and a total of 9 cubes were cast of each mixture as shown in Figure 8. The reason for this was that for each measurement, 3 cubes were used in order to get an average compression strength. The measurements were done after 1,7 and 28 days. The results from these measurements are shown in Figure 26.

Figure 9: Concrete with no plasticiser.

Figure 10: Concrete with too much plasticiser.

Sample	**Ingredient**	**Weight (kg)**
Standard	OPC	4
	Limus 25	4
	Gravel	21,56
	Small stones	14,374
	ACE Glenium 51	0,04
	Water	3,6
Cyclone ash (30 mass%)	OPC	4
	Limus 25	2,8
	Gravel	21,56
	Small stones	14,374
	ACE Glenium 51	0,06
	Water	3,6
	Ash	1,2
Cyclone ash (50 mass%)	OPC	4
	Limus 25	2
	Gravel	21,56
	Small stones	14,374
	ACE Glenium 51	0,04
	Water	3,6
	Ash	2
Wood ash (30 mass%)	OPC	4
	Limus 25	2,8
	Gravel	21,56
	Small stones	14,374
	ACE Glenium 51	0,1
	Water	3,6
	Ash	1,2
Wood ash (50 mass%) (washed)	OPC	4
	Limus 25	2
	Gravel	21,56
	Small stones	14,374
	ACE Glenium 51	0,04
	Water	3,6
	Ash	2
Fly ash (30 mass%)	OPC	4
	Limus 25	2,8
	Gravel	21,56
	Small stones	14,374
	ACE Glenium 51	0,05
	Water	3,6
	Ash	1,2

Table 5: Amount of ingredients being mixed for compressice strength measurements.

6. Results

6.1 Cyclone ash

6.1.1 Vicat measurements of cyclone ash

Whilst performing the first measurement of OPC with 10 mass% of cyclone ash the paste started to swell. This swelling occurred fast, as can be seen in Figures 12, 13 and 14. When the mould was taken out and the paste removed the texture was porous and soft. The decision was then made to wash the ash, as mentioned in chapter 5.2.1, to make it possible to perform the Vicat test.

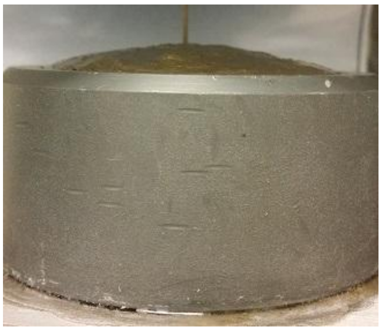

Figure 11: After 55 minutes.

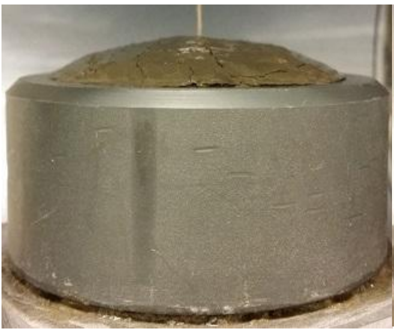

Figure 12: After 1 h, 30 minutes.

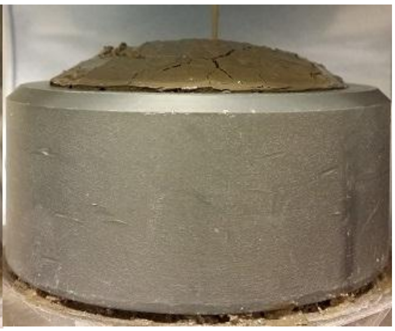

Figure 13: After 2 h, 25 minutes.

A new Vicat test was run with 10 mass% cyclone ash that had been 18 hours in the same water as it was to be cast in. The ash had swelled in the water and a swirl caused a gas to be released. The new Vicat test did not show any sign of swelling.

In the test with 30 mass% cyclone ash that had been washed for 16 hours the paste did swell again. Not as much as with the 10 mass% unwashed cyclone ash but enough so that the needle began to scrape the surface of the paste. Therefore a longer time of washing was performed in 200 grams of water as described in chapter 5.2.1. After this time the tests could be performed.

For the 50 mass% cyclone ash, most of the water the ash had been washed with were accidentally spilled and was replaced with distilled water. Again the paste slowly started to swell. Before the end of the program a top layer had to be removed, as seen in Figure 14, so the sample would not swell enough to touch the needle.

Figure 14: Top layer of 50 % cyclone ash mixture have been removed and shows holes in the paste.

Figure 15 shows the comparison between the Vicat test and calorimetry measurements regarding cyclone ash. With an increased amount of washed ash the time for the paste to start to harden also increases. The length of the program was not enough to measure exactly when the 50 mass% washed cyclone ash began to harden. When removing the paste from the mould the texture was beginning to lose plasticity.

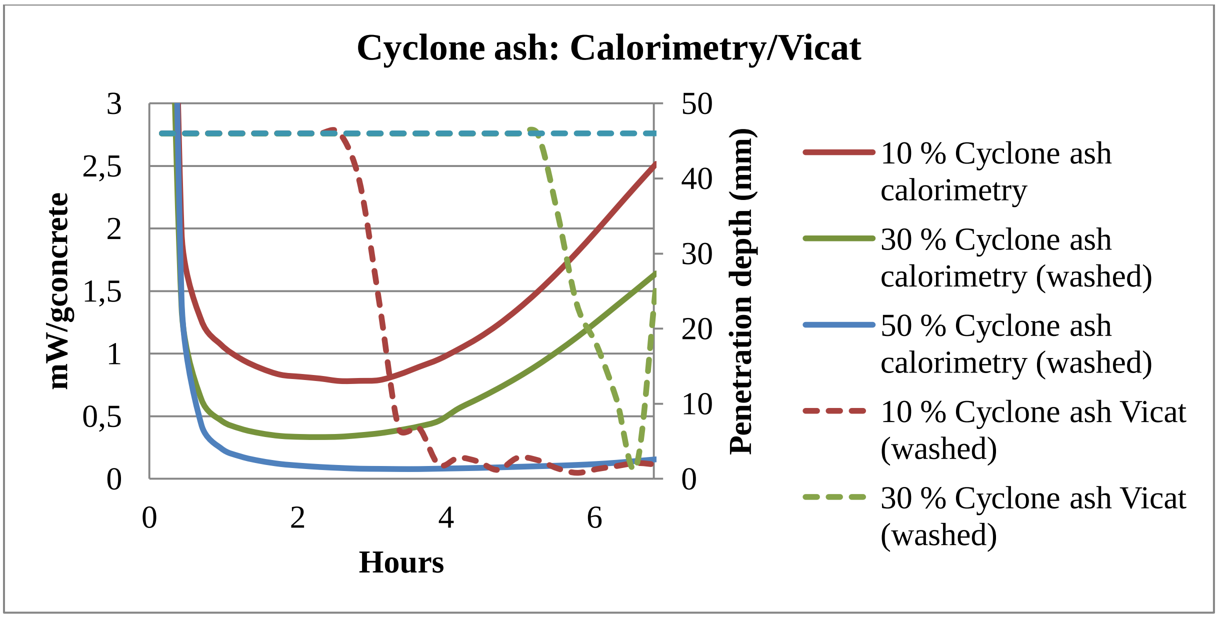

Figure 15: Comparison between calorimetry and Vicat data for OPC mixed with different mass% of cyclone ash

6.1.2 Isothermal calorimetry measurements of cyclone ash

The unwashed cyclone in Figure 16 gave of most energy during the calorimetry measurements compared with the other ashes, see Figures 28 and 38.

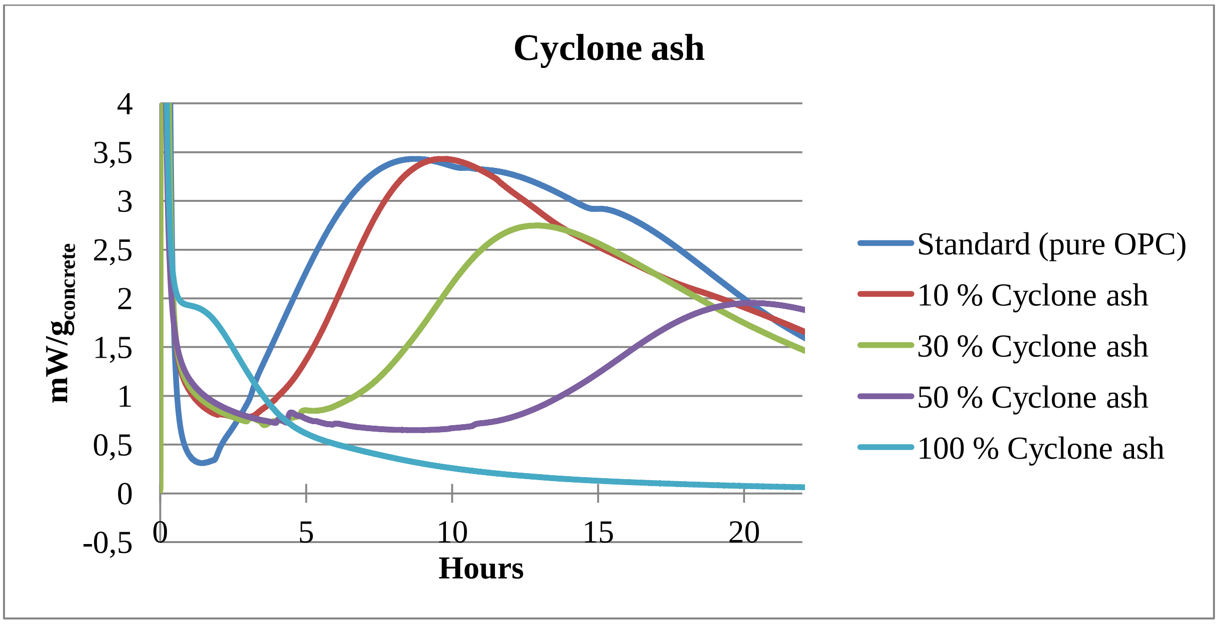

Figure 16: Calorimetry data of pure OPC and different cyclone ash/OPC mixtures in mass%.

Figure 17 visualise the difference between washed and unwashed cyclone ash. The calorimetry curves shows that the energy release happened quicker with the washed ash, than with the unwashed ash, but the amount of energy was not as high.

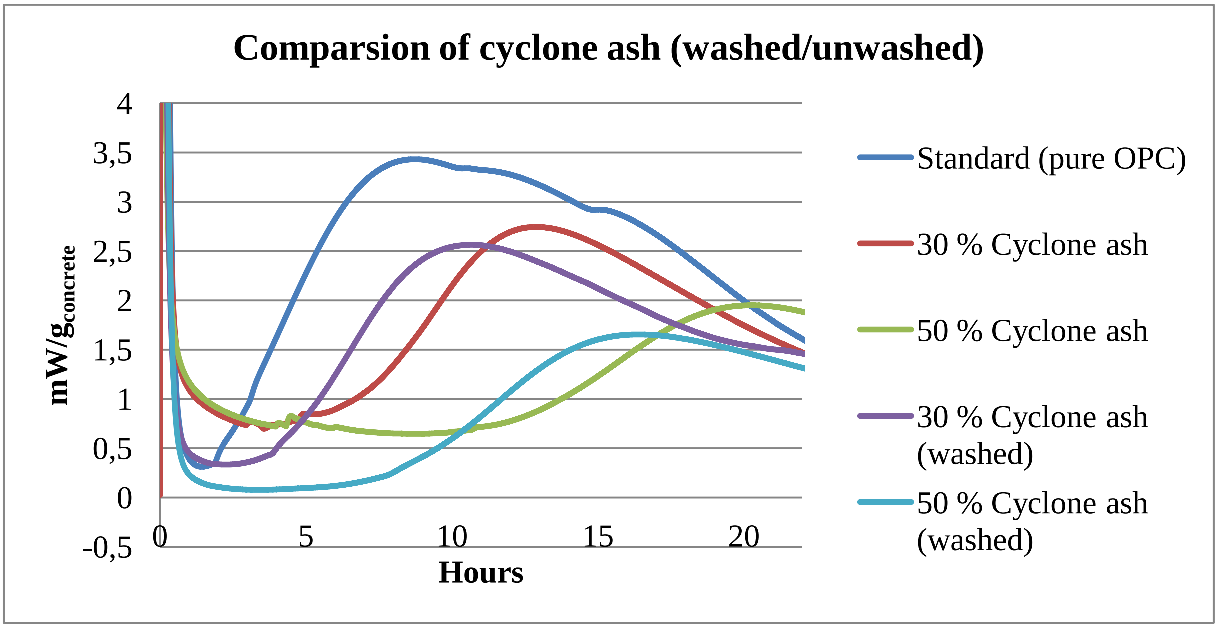

Figure 17: Comparison of calorimetry data between 30/50 mass% washed/unwashed cyclone ash mixtures with pure OPC.

Tests were also conducted on how the energy release would look on a longer timescale. In Figure 18 the unwashed ash showed a high energy release. In Figure 19 the washed 30 mass% ash showed a second energy release that started around 30 hours which were almost as high as its first top. The 50 mass% did not show any new energy release in the measured time span.

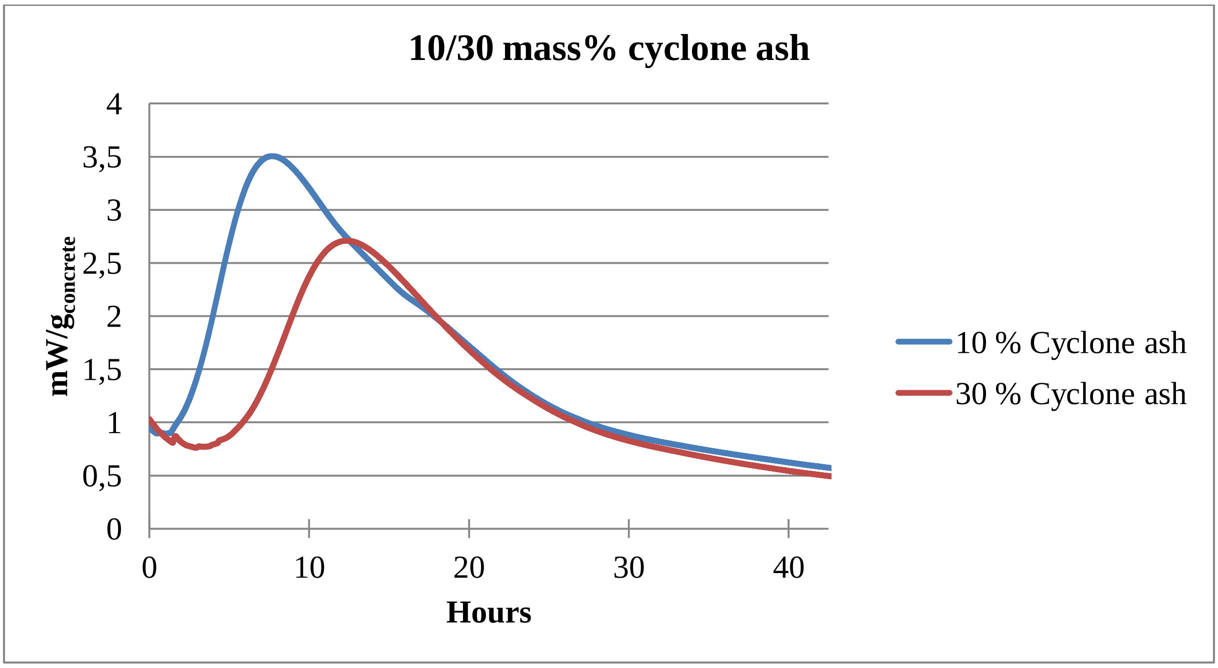

Figure 18: Long calorimetry data collection of 10/30 mass% cyclone ash/OPC mixtures.

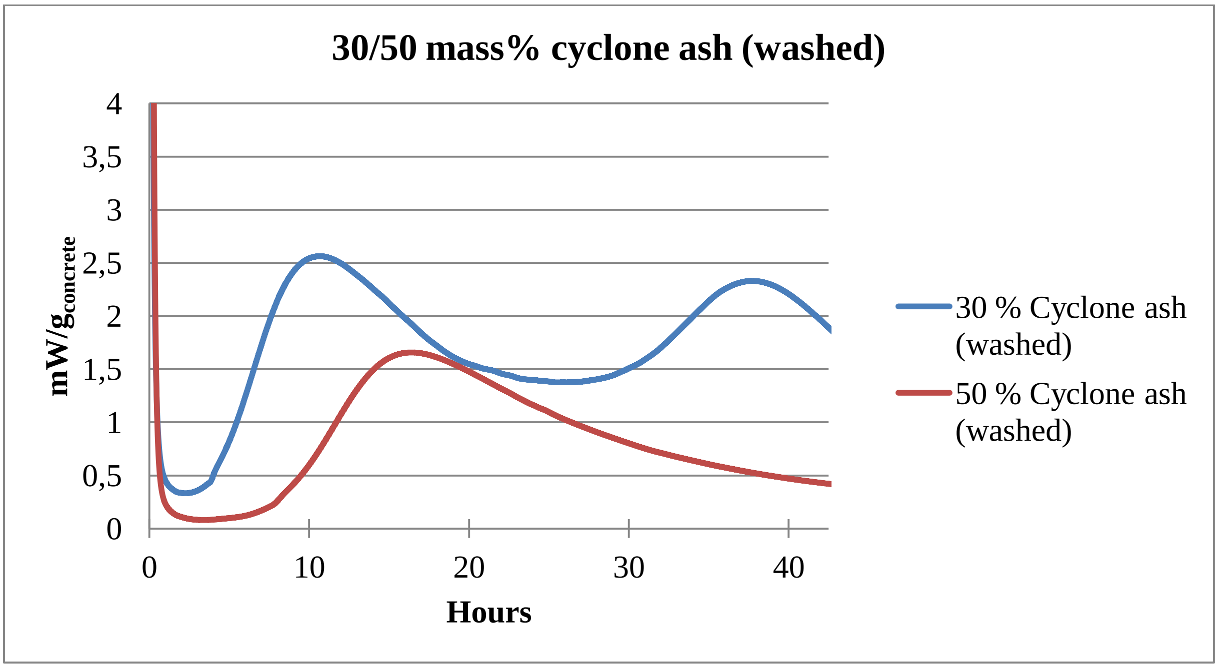

Figure 19: Long calorimetry data collection of 30/50 mass% washed cyclone ash/OPC mixtures.

6.1.3 Infrared spectroscopy measurements of cyclone ash

All spectroscopy graphs in this report are calculated by taking the measured spectrum at a desired time and subtract the very first spectrum measured in the beginning. A decrease in intensity means that a substance is disappearing and a increase means that a substance are created. Figures 21-26 show the infrared spectroscopy measurements of cyclone ash. To make it easier to compare visually between the washed and unwashed samples, these are placed next to each other in Figures 22-25.

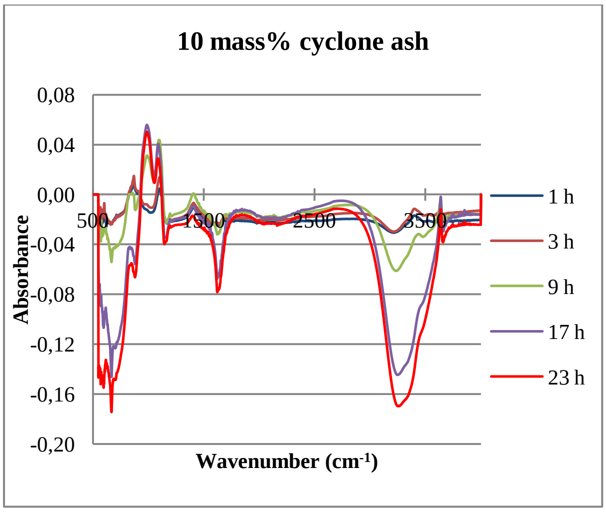

Figure 20: Infrared spectroscopy of 10/90 mass% of cyclone ash/OPC. Reference time is 4 minutes.

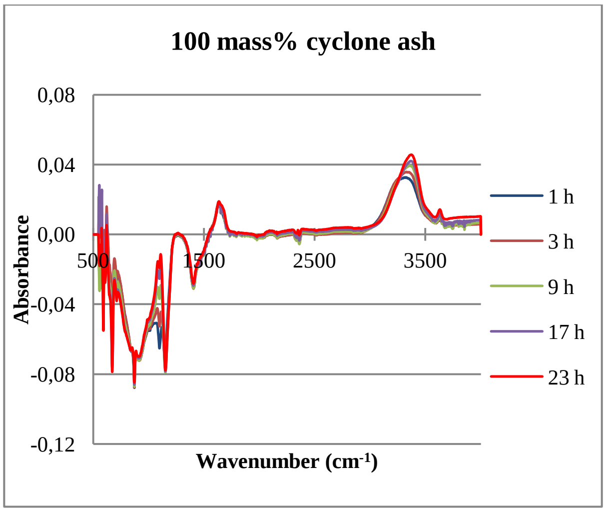

Figure 21: Infrared spectroscopy of 100 mass% of cyclone ash. Reference time is 4 minutes.

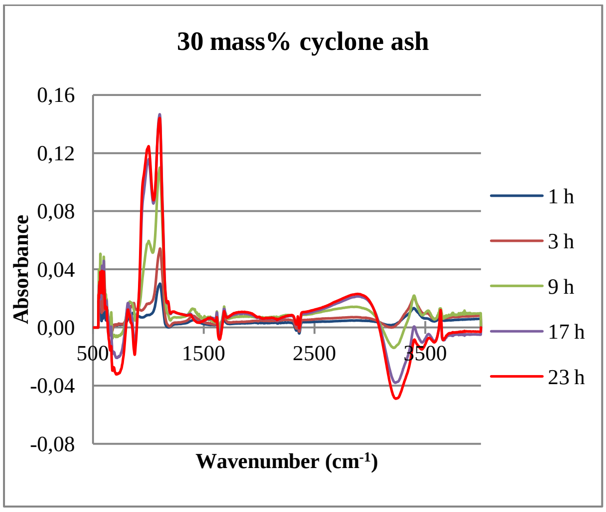

Figure 22: Infrared spectroscopy of 30/70 mass% of cyclone ash/OPC. Reference time is 4 minutes.

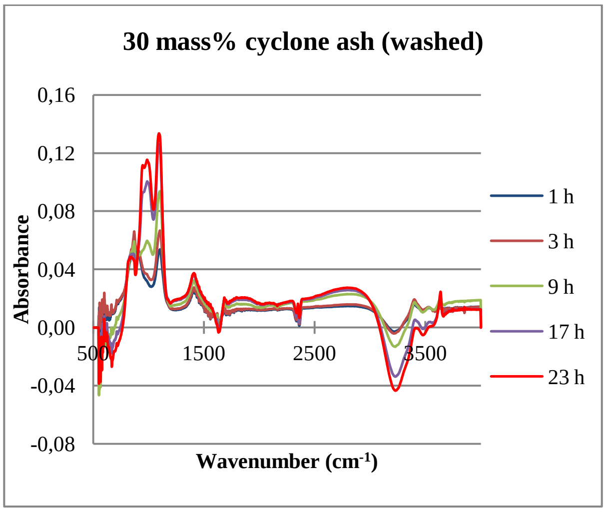

Figure 23: Infrared spectroscopy of 30/70 mass% of washed cyclone ash/OPC. Reference time is 4 minutes.

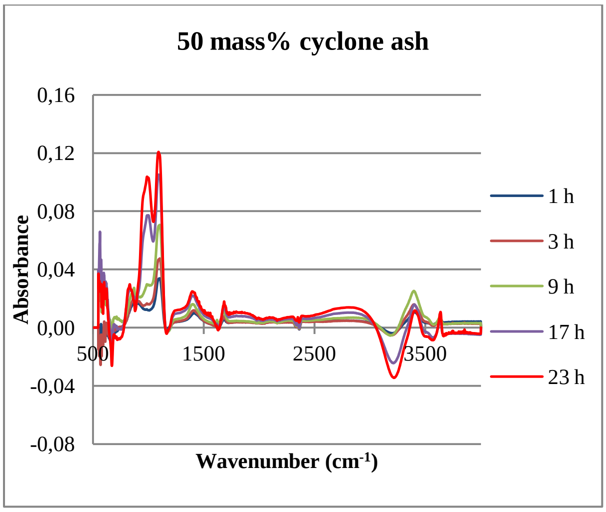

Figure 24: Infrared spectroscopy of 50/50 mass% of cyclone ash/OPC. Reference time is 4 minutes.

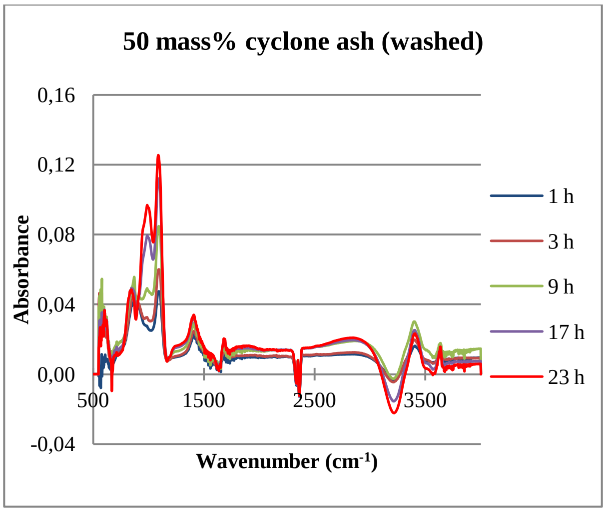

Figure 25: Infrared spectroscopy of 50/50 mass% of washed cyclone ash/OPC. Reference time is 4 minutes.

Figure 20 show that there is much change around ~550-1100 cm^{-1}, ~1600 cm^{-1} and ~3000-3600 cm^{-1}. In Figure 21 there are some change in the peaks, most notably around ~550-800 cm^{-1}, ~1000 cm^{-1} and ~3400 cm^{-1}.

6.1.4 Compressive strength measurements of unwashed cyclone ash

The compressive strength measurements of cyclone ash concrete (black and red) in Figure 26 shows a weaker build-up of strength compared with the other ashes. The cyclone ashes in Figure 26 are unwashed and is missing data on the strength development after 1 day. The reason of this is because of the swelling which made it difficult to measure the cubes.

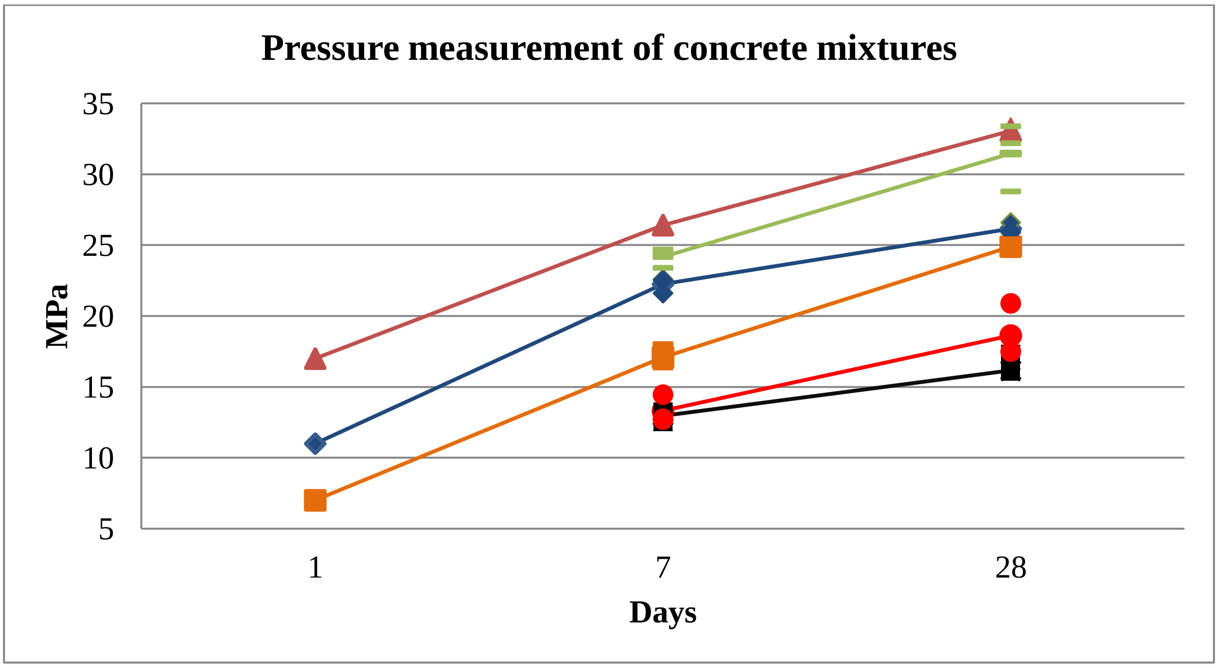

Figure 26: The drawn lines in the figure represents the average strength and the dots represent the data given when the cubes were compressed. There are no individual data from day 1, only the average strength. Measurement of pressure strength of different concrete mixtures: blue=standard, green=30 mass% wood ash, crimson=50 mass% wood ash (washed), black=30 mass% cyclone ash, red=50 mass% cyclone ash and orange=30 mass% fly ash.

The concrete containing 30 mass% of cyclone ash had the smallest strength development and the measurements had a small spread. Concrete with 50 mass% of cyclone ash was a little better but the measurement values were spread more.

6.2 Wood ash

6.2.1 Vicat measurements of wood ash

Figure 27 shows the comparison between the Vicat tests and calorimetry measurements for wood ash.

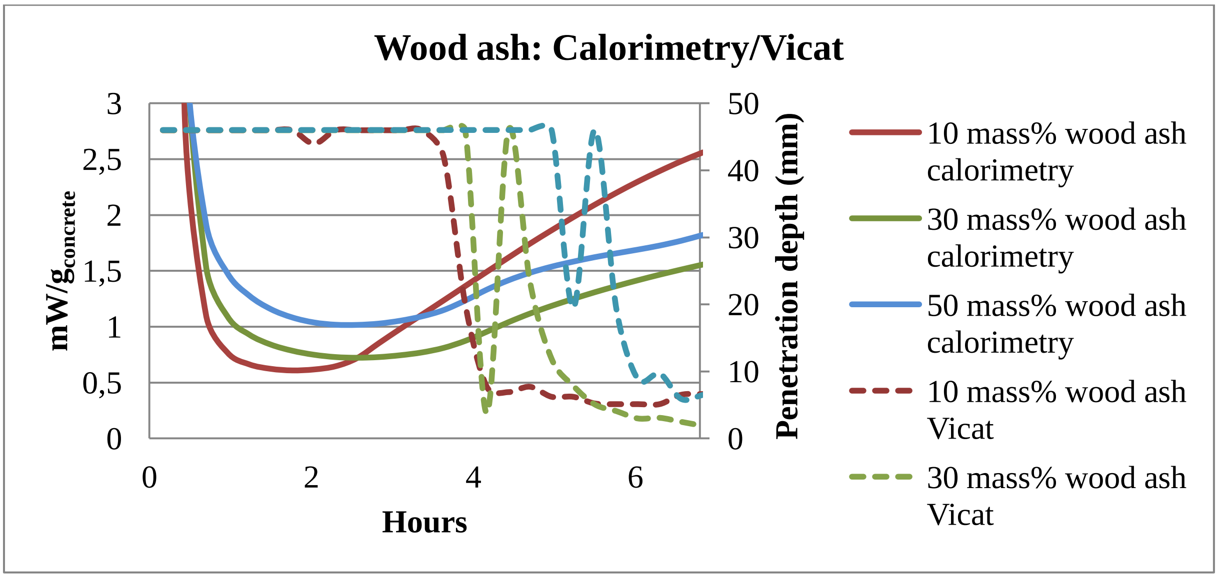

Figure 27: Comparison between calorimetry and Vicat data for different mass% of wood ash/OPC mixtures.

In Figure 27 the small bumps on the calorimetry curve, that are more easily seen for the standard in the Appendix Figure 45 after 2 hours and respectively for the cyclone ash in Figure 15, also occur roughly at the same time as the mixture with wood ash begins to harden.

6.2.2 Isothermal calorimetry measurements of wood ash

The calorimetry curves in Figure 28 shows that 10 mass% and 50 mass% mixtures have a quicker energy release than 30 mass%.

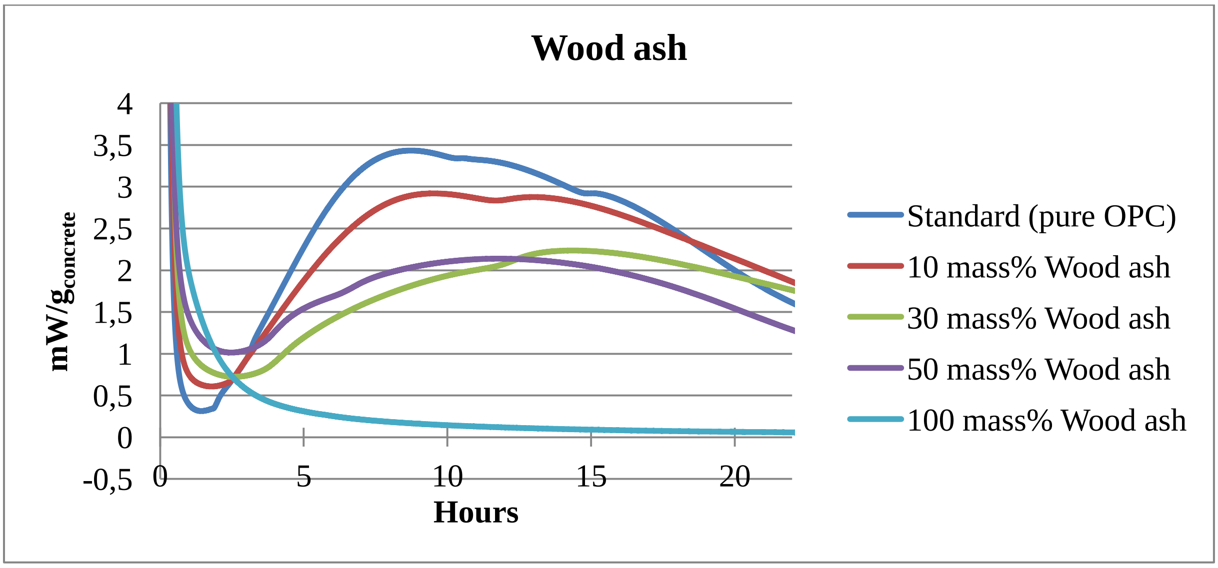

Figure 28: Calorimetry data of different wood ash/OPC mixtures in mass%.

6.2.3 Infrared spectroscopy measurements of wood ash

Figures 30-33 shows the spectroscopy measurements of wood ash mixed with OPC.

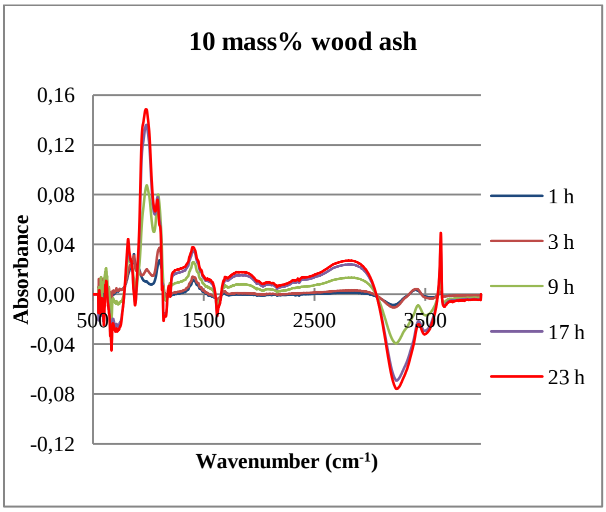

Figure 29: Infrared spectroscopy of 10/90 mass% of wood ash/OPC. Reference time is 4 minutes.

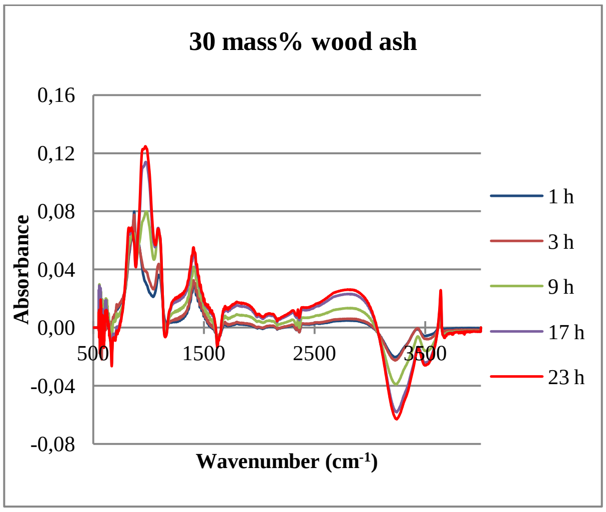

Figure 30: Infrared spectroscopy of 30/70 mass% of wood ash/OPC. Reference time is 4 minutes.

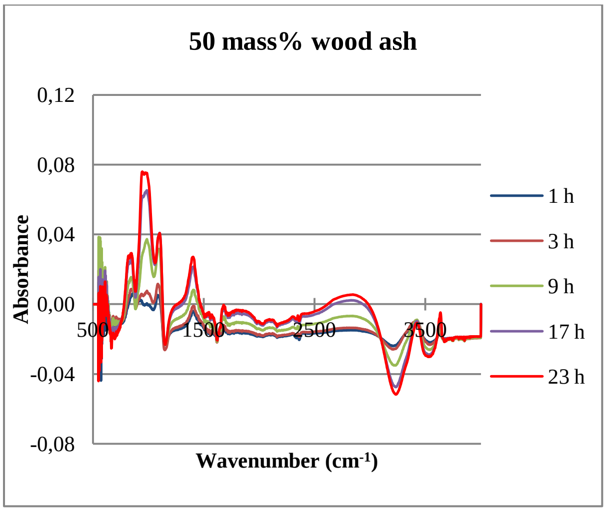

Figure 31: Infrared spectroscopy of 50/50 mass% of wood ash/OPC. Reference time is 4 minutes.

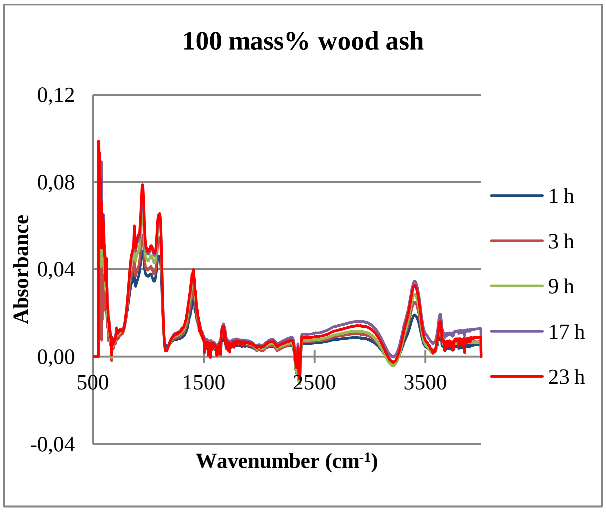

Figure 32: Infrared spectroscopy of 100 mass% of wood ash. Reference time is 4 minutes.

6.2.4 Compressive strength measurements of wood ash

Wood ash was the most water demanding ash that was tested which is discussed in chapter 5.2.1. In Figure 33 the effects of the water absorption of the ash when a insufficient amount of water is applied to the mixture is clearly visible.

A single cube, 30 mass% wood ash concrete, had been taken out of the mould and the aggregates are clearly visible in Figure 33. The dark colour comes from the fact that the cube is wet, not due to the colour of the ash. In Figure 34 the mixture is laid out and there is no plasticity in the paste and it seems that there are just aggregates and ash mixed. To compare visually, Figure 35 and 37 respectively show cubes of standard concrete and concrete paste with good plasticity.

Figure 33: Cube with 30 mass% wood ash.

Figure 34: Paste with 30 mass% wood ash.

Figure 35: Cube of standard concrete.

Figure 36: Paste of standard concrete.

In Figure 26 the wood ash (green and crimson) showed the best strength development as it is higher than the standard. The washed ash has the highest strength and the measurement data are close to the value of the average. The unwashed ash has no 1 day measurement due to the large content of unburnt coal which made it crumble. 7 and 28 days measurement shows a bigger spread around the average value.

6.3 Fly ash

6.3.1 Vicat measurements of fly ash

Figure 37 shows the comparison between the Vicat and calorimetry measurements.

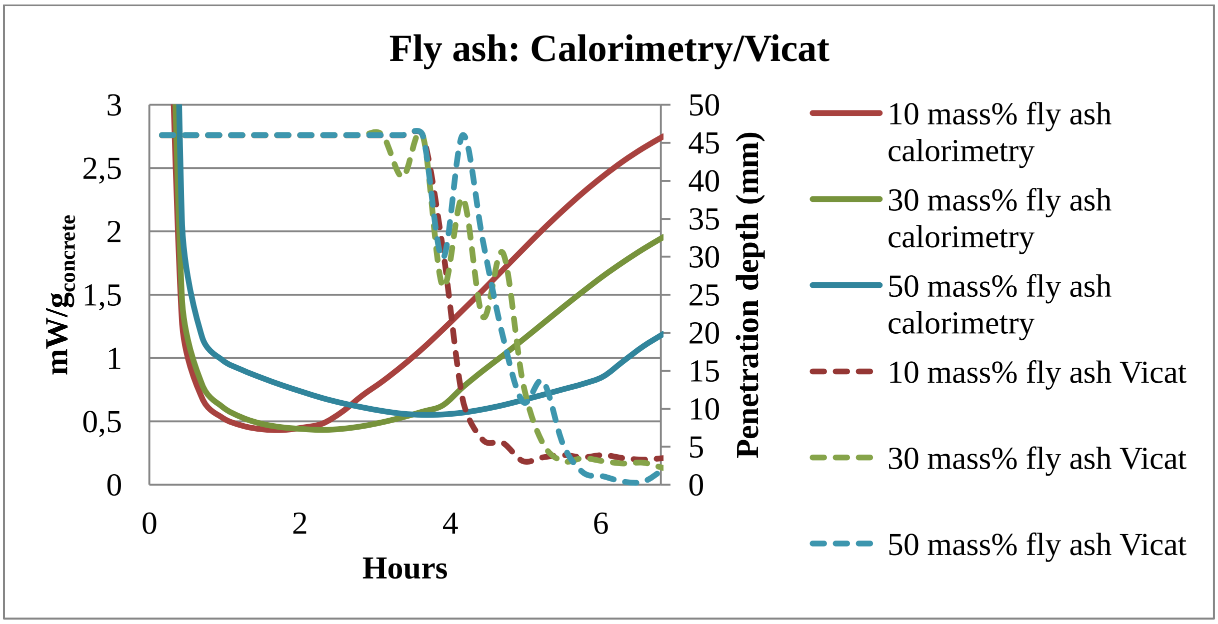

Figure 37: Comparison between calorimetry and Vicat data for different mass% of FLY ASH ash/OPC mixtures.

6.3.2 Isothermal calorimetry measurements of fly ash

Calorimetry measurements showed that with an increasing amount of ash, in Figure 38, the total energy realease decreased and the time for this release increased.

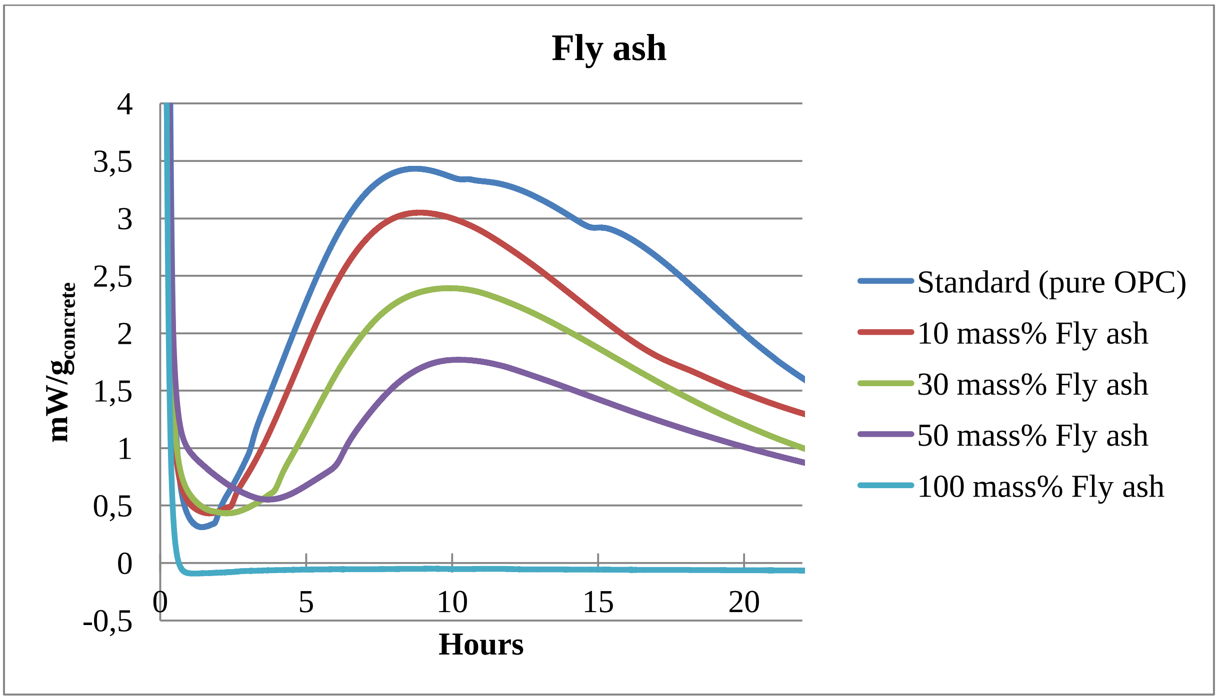

Figure 38: Calorimetry data of pure OPC and different fly ash mixtures in mass%.

6.3.3 Infrared spectroscopy measurements of fly ash

The spectroscopy measurements for fly ash measurements are shown in Figures 40-43.

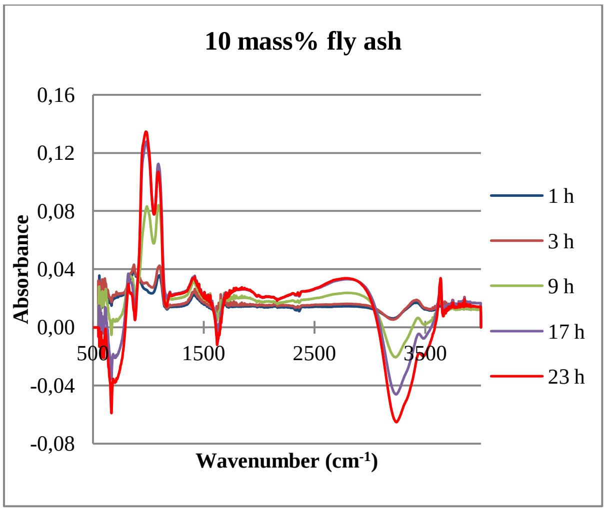

Figure 39: Infrared spectroscopy of 10/90 mass% of fly ash/OPC. Reference time is 4 minutes.

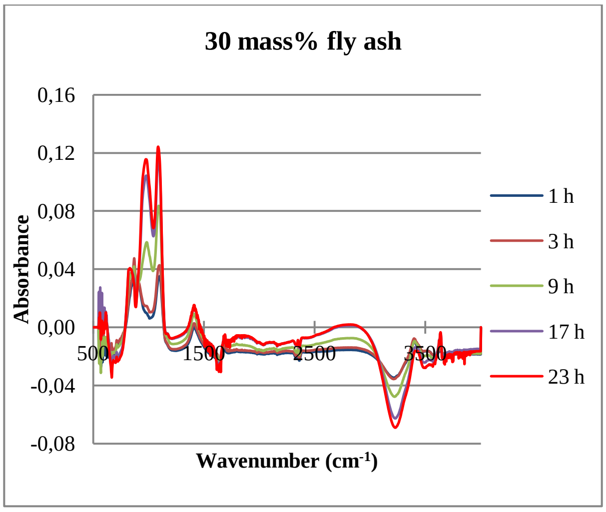

Figure 40: Infrared spectroscopy of 30/70 mass% of fly ash/OPC. Reference time is 4 minutes.

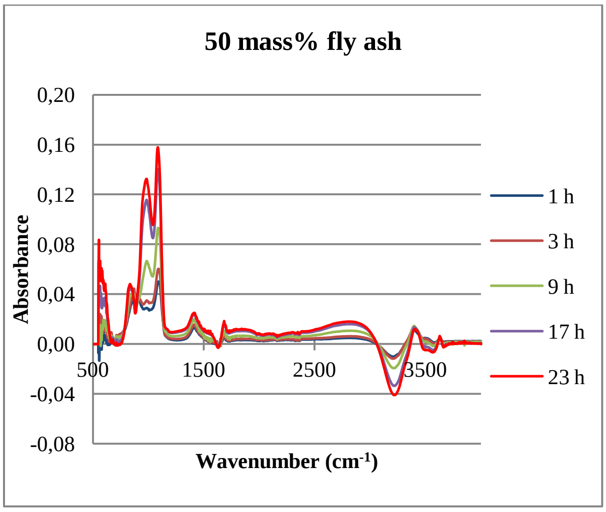

Figure 41: Infrared spectroscopy of 50/50 mass% of fly ash /OPC. Reference time is 4 minutes.

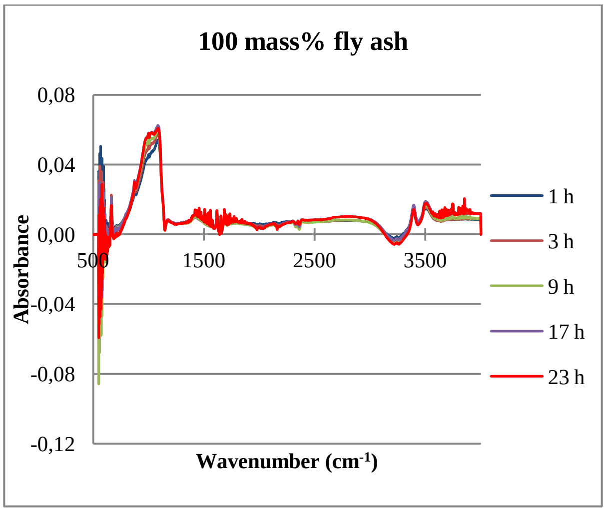

Figure 42: Infrared spectroscopy of 100 mass% of fly ash. Reference time is 4 minutes.

Figure 42 shows that the only noticable changes occured around ~600 cm^{-1} and ~1100 cm^{-1} and a small decrease around ~650 cm^{-1} and ~1000 cm^{-1}.

6.3.4 Compressive strength measurements of fly ash

The build up of strength in concrete containing fly ash in Figure 26, showed a initial weak strength but the strength steadily increased and got closer to the standard concrete. There was little spread between the values.

7. Discussion

7.1 Cyclone ash

A quick gaseous reaction with this ash when it came into contact with water caused a high energy release which in turn may explain why the paste started to swell. This may be due to the fact that there may be aluminium in this ash since the fuel is household waste. That there was something reacting in the ash is also shown in Figure 16, in that the energy release of 100 mass% cyclone ash happened quicker than ash mixed with OPC. Aluminium reacts with the hydroxides and releases hydrogen gas. When the ash had been washed in water for the 10 mass% measurement a swirl of the bowl caused a gas to be released. This was the hydrogen gas so the ash reacts as soon as it comes into contact with water. This effect made the unwashed ash unsuitable to perform any Vicat test with since this paste swelled so much that it risked to destroy the needle in Vicat machine if the paste would begin to harden.

It was enough to wash 10 mass% cyclone ash in the amount water needed to have the w/c ratio of 0,4 but the problem of swelling came back when more ash was added. The amount of water or the time the ash spent in water maybe affected if the ash would cause a swelling or not. But by washing the cyclone ash it showed an effect on the hydration process as can be seen in the difference between measurements on washed and unwashed cyclone ash.

When performing the 50 mass% measurement in the Vicat machine the top layer had been removed. The paste had holes in it that probably was pockets of gas, as seen in Figure 14 which means that there still was unreacted aluminium in the ash after the washing. These pockets weakens the concrete even if it hardens given time. These results show that to make use of cyclone ash without a thorough washing can cause problems with gas developments.

The calorimetry curve in Figure 15 is for unwashed 10 mass% cyclone ash but the Vicat curve is for washed 10 mass%. In order to do a estimation if the calorimetry curve for washed 10 mass% cyclone ash begins to rise at the same time as the paste begins to harden, the effects on the calorimetry curves for unwashed ash and washed ash can be seen in Figure 17. A washed ash reaches a lower energy at first and is followed by a quick rise in energy release. This means that the curve is pushed down and moves slightly to the left. With this in mind the imagined curve for washed 10 mass% cyclone ash would begin to rise approximately at the same time as the hardening process began in Figure 15.

In Figures 19 and 20 longer measurements were taken. As expected, due to the probable contents of reactive aluminium, the unwashed ash had a higher energy release than the unwashed ash. The interesting observation made is that if the ash had been washed and mixed with cement, it showed a new energy release that began around 30 hours after it had been mixed. This was only observed for the 30 mass% washed ash and no such release for 50 mass% washed ash, at least not during the time that the measurements were taken. It can only be speculated what might cause this and what effects this might have on the strength development since there is only the calorimetry data to observe.

The strength development in Figure 26 show no data on 1 day since it was not feasible to perform a measurementdue to the swelling and texture of the concrete. Since there are data on 7 and 28 days it might suggest that the concrete was hard enough by then, to make it possible to chip off parts that had swelled over the side of the cubes. The cyclone ash mixtures that were cast at CBI were not washed. It would have been interesting to see the strength development of washed ash in the compression measurement.

What can be seen is that in Appendix, Figure 45, when pure OPC was tested in Vicat and compared with calorimetry measurements there were two small changes or bumps in the calorimetry curve. These bumps occurred just after 2 hours and again at 3 hours. These changes may have something to do with the hardening of the cement since they seem to occur at the same time. These small changes also occur in cyclone ash, see Figure 15. If applying the reasoning three paragraphs earlier, the curve change of the calorimetry happens at the same time as the concrete begins to harden. In Figure 17 the small change in the curve for 50 mass% washed ash is at around 8 hours after mixture, too long for the Vicat to measure this. So in cement mixed with washed cyclone ash there is a retarding reaction that effects the beginning of the hardening phase.

Figure 20 show a decrease of substances around the wavenumbers in cm^{-1} of 550-900, 1100, 1400-1700 and 3000-3600. It also show that there was an increase around the wavenumber for polymerized silica. In Figure 21 the wavenumbers suggest a formation of polymerized silica and capillary water respectively.

Figures 22-25 shows that the unwashed and washed cyclone ash mixtures look almost the same, except that there seem to be an increase around ~550 cm^{-1} that can be explained by a decrease in intensity, in all but for the washed 30 mass% cyclone ash. The unwashed 30% cyclone ash did not show a peak at ~1400 cm^{-1}. Also a more noticeable decrease ~ 2400 cm^{-1} is observed.

As can be seen in Appendix, Figure 43, pure OPC shows a peak around 3600 cm^{-1} that indicates $Ca(OH)_2$ formation. There were no such distinct peaks in any of the cyclone ash mixtures, be they washed or unwashed as seen in Figures 20-25. Since calcium hydroxide forms C-S-H with pozzolanic materials the small amount of calcium hydroxide produced may not have been enough for this to occur. The washed ash showed a smaller growth of $CaCO_3$. At ~1400 cm^{-1} may be C-S-H and ~2800-3300 cm^{-1} shows water that have been cristallized. 100 mass% unwashed ash showed that reactions occur when the ash was mixed with water. These reactions were mainly around the wavenumbers of polymerized silica, capillary water and $CaCO_3$.

A general comparison between the spectroscopy and calorimetry measurements showed that the consistent change was ~2800 cm^{-1}, were the washed ash did not increase in intensity after 9 hours compared to the unwashed ash. At around that time the energy release almost peaked for the washed ash whiched happend later for the unwashed ash.

7.2 Wood ash

This ash had the largest need of water. The calorimetry curves in Figure 28 show that the energy release is roughly the same as for the other mixtures. The difference being that for 10 and 30 mass% the energy release seems to "die" out more slowly. Especially for the 30 mass% mixture curve that is decreasing slower than the others. The energy release seems to continue for a longer time period at a higher level.

The changing of the w/c ratio for this ash was needded to increase the workability of the mixture. When mixing the 50 mass% sample for the Vicat the paste seemed to be too fluid for it to have time to harden before the measurement time was over. However when the measurement was over it showed that the paste had hardened as seen in Figure 27. The reason why the Vicat curve seems to shift between less or more hard, could be due to the fact that the ash contained some larger unburned coal particles. They may unfortunately have acted together and formed clumps and creating a bigger obstacle inside the paste. This could cause it to seem to be a quicker setting at certain points. But the general trend is that there is a delayed setting period the more ash there is in the concrete.

The Figure 27 show small changes in the calorimetry curve that seem to occur around the same time as the paste starts to harden. The higher the amount of ash in the cement, the longer it takes for the cement to start to harden. The difference is not as big as the one observed when measuring washed cyclone ash. With each increase of 20 mass% ash the delay for the hardening to occur was roughly one hour.

Whilst performing the measurements at CBI it was shown that unwashed ash required more plasticiser than washed ash in order to be able to cast. When the ash was washed there was considerable improvement on the plasticity of the paste and less of ACE Glenium 51 was needed. Unwashed ash did crumble when the strength test was performed after 1 day but after a longer time of hardening it did not crumble and could then be measured. The ash also showed a good strength development during the compression tests in Figure 26, both the washed and unwashed ash. More so than the other mixtures which all were lower than the standard. This shows that the usage of ashes with a high amount of unburnt carbon can be beneficial for making a strong concrete.

In the spectroscopy measurements there was a high peak around ~1400 cm^{-1} in the 30 and 50 mass% mixture, which may be C-S-H, relative to the other ash mixtures. For all wood ash samples there were an increase around ~1000 cm^{-1} and ~2300-2800 cm^{-1}. All of them exhibited a decrease around ~2800-3300 cm^{-1}. 100 mass% wood ash, Figure 32, there were an increase between ~700-1000 cm^{-1}, ~2300-2800 cm^{-1} and ~3400 cm^{-1}. The highest formation of $Ca(OH)_2$ appeared in the 10 mass% wood ash sample. But as the ash content got higher this peak became smaller, probably due to that more and more calcium hydroxide reacted with the carbon in the ash.

A comparison between the spectroscopy and calorimetry measurements showed no clear difference between the mixtures even if the energy release happend earlier in the 50 mass% than in the 30 mass%.

7.3 Fly ash

Performing the Vicat test with the fly ash was the least problematic of the three ashes tested. No preparation was needed except either drying or calculating absorbed water, when it came to the w/c ratio. The plasticity of the mixture did increase as the mass% increased. The interesting observation that can be seen in Figure 37 is that, even if the plasticity and the workability became easier with an increasing amount of ash, the setting time for all three mixtures were almost equal. Even if the energy release for each mixture decreased this seems to have no effect on when the paste started to harden. This can be interpreted as the ash is acting as a filler material.

The small bumps that was observed for the cyclone ash in Figure 15 or the standard in Appendix, Figure 45, do not seem to occur simultaniously in the fly ash. Meaning that when the paste started to harden in the standard sample and cyclone ash it showed small bumps which in the fly ash did not occur at the same time. For 50 mass% of fly ash this small change even takes place after the cement paste has hardened. The Vicat measurements in Figure 37 also shows a behavior similar to that of wood ash as the hardening jumps up and down. This may be due to a similar problem to that of wood ash that there may be some particles in the ash that sticks together and form a obstacle. Even some places of the mixture may contain less of these particles making the paste softer. But the general trend is that the hardening occurs almost at the same time for each of the tested mixtures.

The interesting thing that can be seen in Figure 38 is the measurement for 100 mass% ash. It was the only curve of all tests that went below 0 so that the energy required to keep the temperature constant became negative. The sample required energy which means that the there were endothermic reactions taking place. Otherwise the calorimetry curves in Figure 38 decreases proportionally when the ash content gets higher. An increasing amount of fly ash clearly lowers the energy release so it has diluting properties. Depending on the temperature whilst casting concrete this can have either positive or negative effects.

Due to lack of material, only one sample of 30 mass% fly ash could be blended and cast at CBI. The strength development of the sample made can be viewed in Figure 26. The mixture is weaker than 30 mass% wood ash, but it follows the same curvature and seem to have a less sloping curve than the 30 mass% wood ash.

The spectroscopy measurement in Figures 40-43 shows that with an increasing amount of ash shows a decrease between ~2500-3000 cm^{-1}. The increase of ash mixed with cement also effected the reactions of substances around ~1600 cm^{-1} and ~3400 cm^{-1}, making reactions here become smaller.

Around ~650 cm^{-1} reactions changed from negative growth at 10 mass% ash to a positive growth at 50 mass% ash. At 10 mass% ash the peak around ~1000 cm^{-1} grew faster than the peak around ~1200 cm^{-1} but at 50 mass% ash the situation was reverse. The formation of $Ca(OH)_2$ was not so big as in pure OPC and it declined from a small peak in Figure 39 to almost become nonexistent in Figure 42.

Figure 42 show the spectroscopy measurement for 100 mass% fly ash. There is hardly any reaction taking place in this ash except small changes around ~650 cm^{-1} and ~1100 cm^{-1}. This is interpreted as fly ash mainly acts as a filler in the cement when taken into consideration the data from Figures 38, 39 and 43.

The spectroscopy and calorimetry measurements showed no big difference when a comparison is done between them, except that with a larger amount of fly ash the peak around ~1100 cm^{-1} got larger even if the energy release decreased.

8. Conclusion

- The hydration of cyclone ash in cement showed that the untreated ash needs to be washed before it is put to use with cement. To use it without washing creates a concrete with a very poor performance.
- By washing the cyclone ash in water the effects of swelling was overcome, atleast for the 10 mass% cyclone ash. The swelling in the later experiments might have been caused by an insufficient amount of water that the ash were washed in .
- Washed cyclone ash showed an extra energy release maximum after about 30 hours. It would have been interesting to see the effect that would have had on the strength development.
- Wood ash was the most water demanding ash of the tested ashes so if the amount of water is a limiting factor this ash would be hard to work with.
- Unwashed and washed wood ash developed the highest strength development of all the tested ashes.
- Wood ash had the largest peaks around ~1400 cm^{-1} which may be C-S-H and can explain why it had the best strength development.
- Concrete with wood ash was one of the ashes that did have a peak of calcium hydroxides that could prevent the effect of carbonation and also create more C-S-H.
- Fly ash was the simplest ash to work with as it did not need more water or any washing.
- Fly ash may be used as a filler alongside cement as the ash did not show any chemcial effects when mixed with cement. This is desirable if the need is to minimize the use of OPC. Also the low energy release is good for avoiding formation of cracks in conrete.

9. Future research

Since large amount of ash from energy plants are being used as landfill, and that the production of cement is energy consuming, the possibility of making use of ashes in concrete is an important subject to look into. I think that future research should be done about the following:

How to better wash cyclone ash and see the effect that it would have in reaction with OPC. If it is possible to decrease the amount of reactive metals in the ash it could improve the performance.

The effects of ashes containing large amounts of unburnt coal and their reaction with OPC since wood ash showed the strongest strength development of the tested ashes.

A deeper study of the strength development of fly ash with OPC. To examine the strength development of concrete, containing fly ash as a filler material, for a longer time period than 28 days.

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Appendix

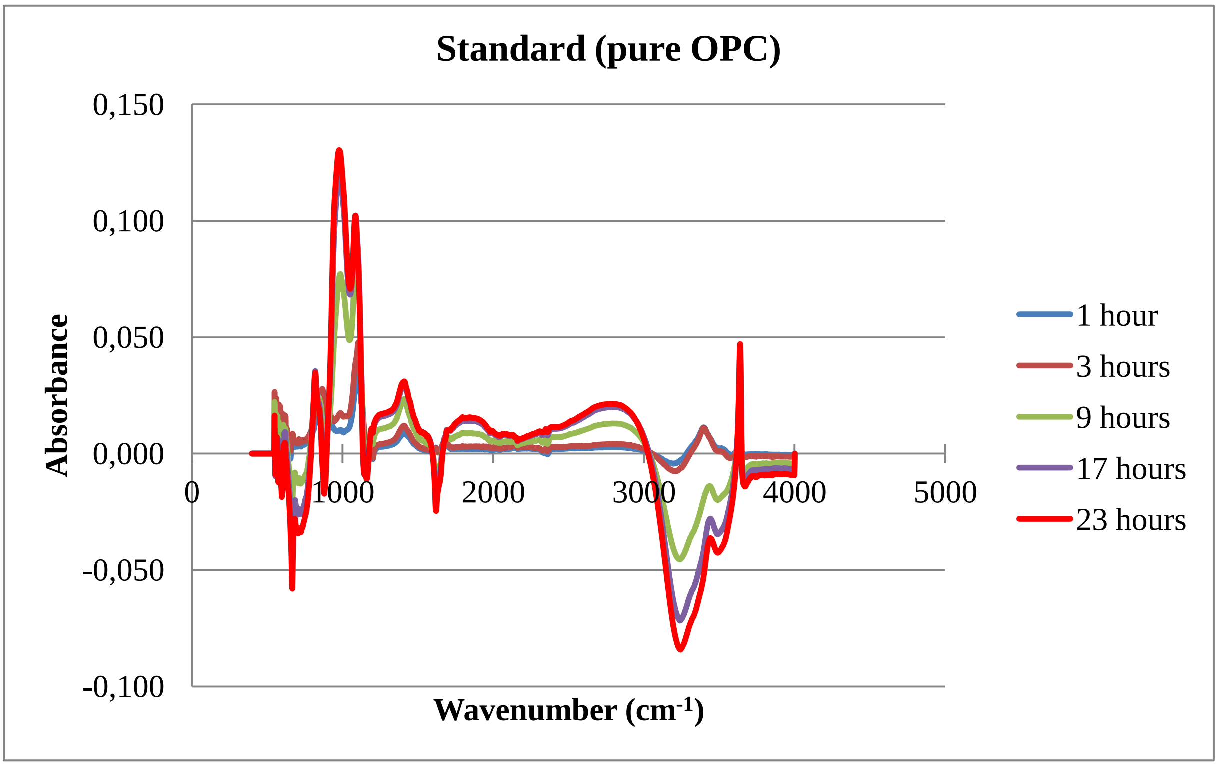

Figure 43: Infrared spectroscopy of pure OPC

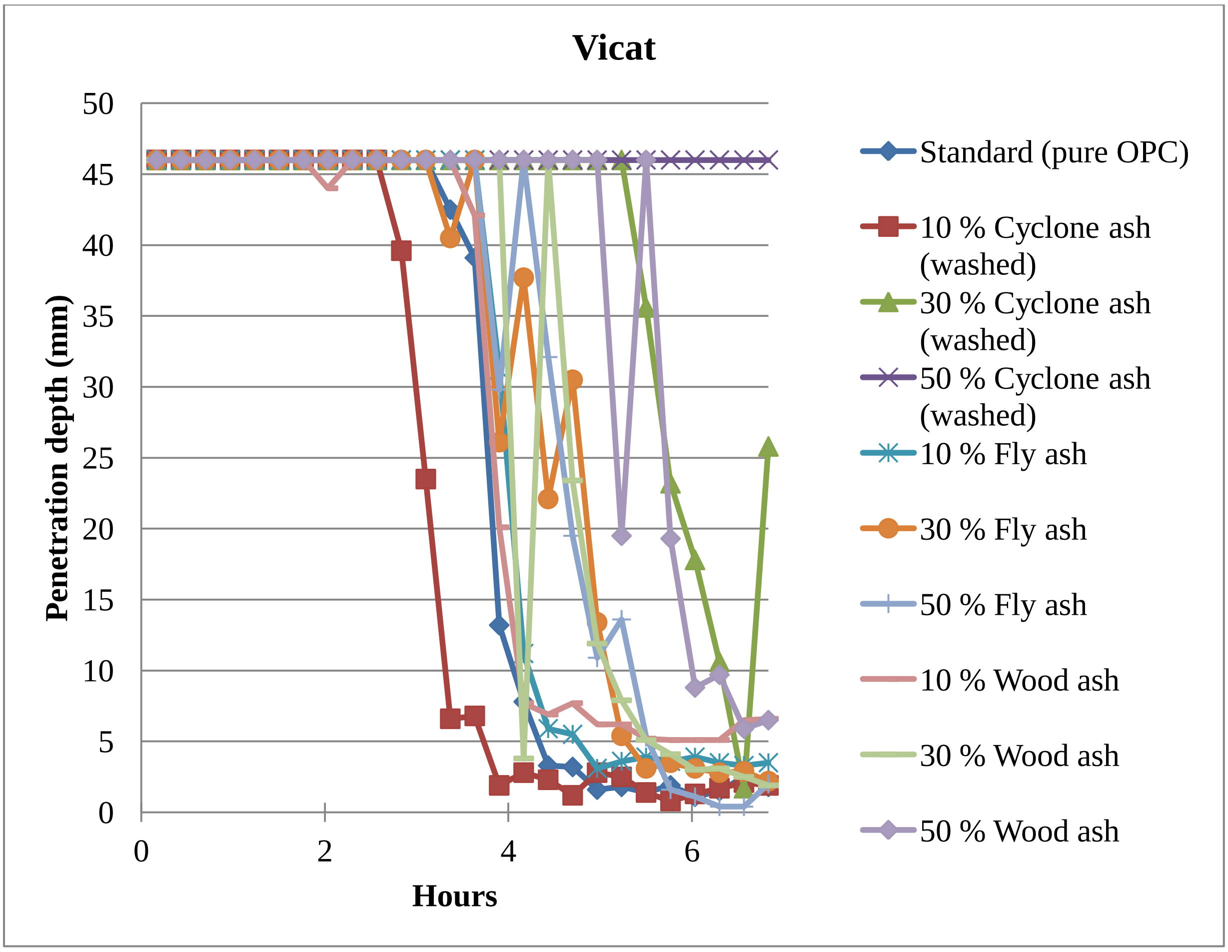

Figure 44: Vicat measurement of all setting times for different concrete/ash mixtures in mass%

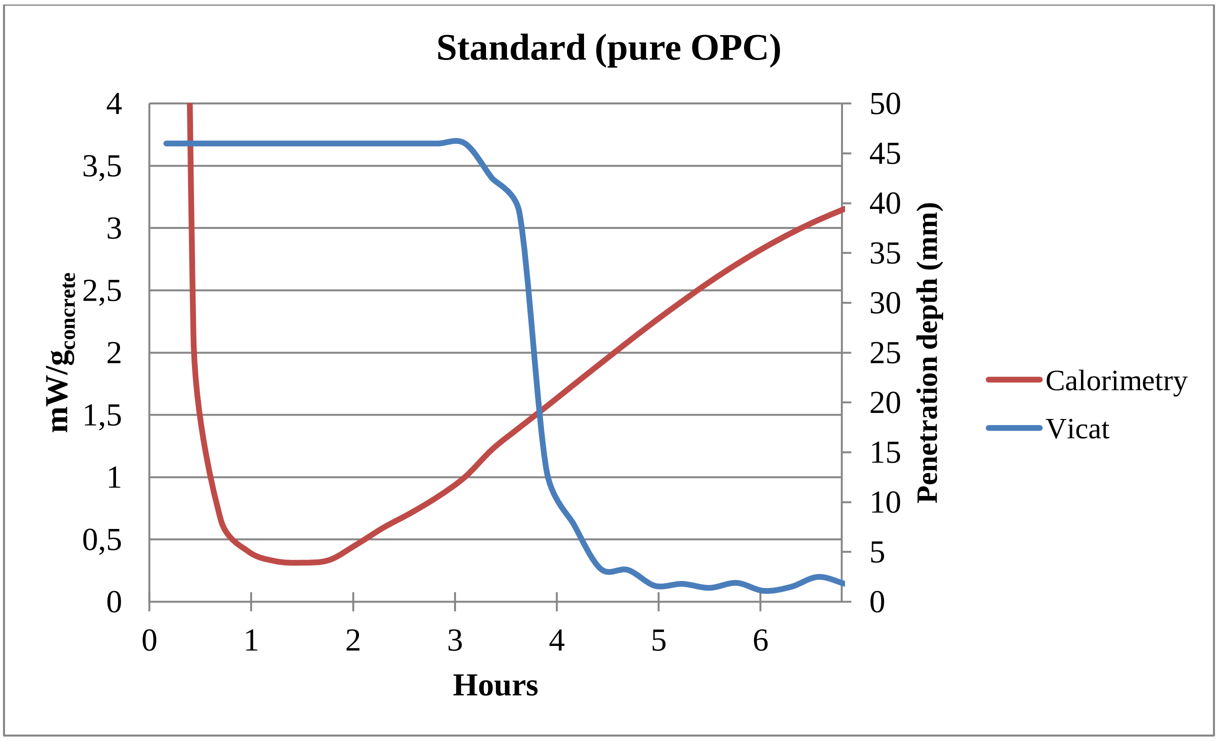

Figure 45: Comparison between calorimetry and Vicat data for pure OPC

Substance	Wood ash
Fe_2O_3	1,99% DS
K_2O	3,57 % DS
MnO	0,887% DS
As	78,2 mg/kg DS
Ba	2250 mg/kg DS
Cd	8,66 mg/kg DS
Hg	0,38 mg/kg DS
Pb	148 mg/kg DS
Sn	7,84 mg/kg DS
V	26,4 mg/kg DS
Zn	3550 mg/kg DS

Table 6: Given contents of the wood ash. DS = Dry Substance