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Temperature effect on performance of Portland cement versus advanced hybrid cements and alkali-Fly ash cement

Tesis Doctoral

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Nomenclature

Nomenclature used in cement chemistry

C = CaO

S = SiO₂

A = Al₂O₃

$\bar{S}$ = SO₃

H = H₂O

F = Fe₂O₃

N = Na₂O

CH = Ca (OH)₂

C-S-H = Calcium Silicate Hydrate

N-A-S-H = Sodium Aluminosilicate Hydrate

OPC = Ordinary Portland cement

Other abbreviations of instrumental techniques / Experiments

XRD: X-Ray Diffraction

XRF: X-Ray fluorescence

XRPD: X-ray Powder Diffraction analysis (Rietveld quantitative analysis of XRD)

MIP: Mercury Intrusion Porosimetry

DTA / TG: Differential Thermal Analysis and Thermo-Gravimetric Analysis

MAS NMR: Magic-Angle Spinning / Nuclear Magnetic Resonance

SEM: Scanning Electron Microscopy

EDX: Energy Dispersive X-Ray

TPB: Three-Point Bending

LVDT: Linear Variable Differential Transformer

SEVNB: Single Edge V-Notched Beam

Resumen

El objetivo principal de este trabajo es estudiar el efecto de la temperatura en diferentes conglomerantes con un bajo contenido de clinker y elevados contenidos de adiciones minerales (“*Supplementary cementitious materials*”, *SCMs*), contenidos superiores a los contemplados en los cementos compuestos (*Blended cement*). Esos nuevos materiales han sido considerados como una de las posibles soluciones para enfrentar el problema ambiental causado por la industria tradicional del cemento, especialmente las emisiones de CO₂.

En concreto los conglomerantes estudiados han sido: i) OPC: cemento Portland comercial tipo CEM I 42.5 como referencia; ii) HYC: cementos alcalinos híbridos preindustrial compuesto de un 30% de clinker de cemento Portland y un 70% de SCMs (mezcla de escoria, cenizas volantes y activador sólido (en diseño); iii) HYP: cemento preindustrial compuesto por un 50% de Clinker de cemento belítico, y 50% de cenizas volantes junto a una pequeña fracción de activador sólido (en diseño); iv) FAN: cenizas volantes activadas alcalinamente (sin Clinker), como activador se empleó una disolución de NaOH 8M (referencia). La investigación se ha centrado en el estudio del efecto de la temperatura en el proceso de hidratación temprana (en el proceso de pre-curado), así como, en el efecto de la exposición de las pastas endurecidas a elevadas temperatura (entre 200 y 1000 °C)

En primer lugar, se estudió como la temperatura de curado en las primeras 20 horas (25 ± 1 o 85 °C d) afecta a la hidratación inicial de estos materiales aglutinantes. Se exploró el efecto de la temperatura de curado inicial sobre la cinética de hidratación y el desarrollo de resistencias mecánicas a 2 y 28 días. También se determinó su efecto sobre los productos de reacción formados y la microestructura desarrollada. Los productos de hidratación formados se caracterizaron usando XRD, SEM/EDX y ²⁷Al y ²⁹Si MAS-NMR. Los resultados obtenidos mostraron que HYC y HYP al hidratarse con agua a temperatura ambiente (25 ± 1 °C) fraguan y endurecen alcanzando unos valores de resistencia mecánica a compresión superior a 30 MPa, a los 28 días. El principal producto de reacción formado fue una mezcla de geles cementosos: C-(A)-S-H y C-A-S-H para HYC y una mezcla de C-(A)-S-H, C-A-S-H y (N,C)-A-S-H para HYP. Curando a 85 °C durante 20 horas, presentaron un comportamiento similar al OPC, inhibieron la formación de ettringita y generaron geles más polimerizados, mejorando la resistencia mecánica de tres días, pero no de 28 o 90 días.

En segundo lugar, en lo que respecta al comportamiento de las pastas endurecidas a elevadas temperaturas (desde 200 hasta 1000 °C), se realizaron dos tipos de ensayos: (1) ensayo para determinar la resistencia mecánica, el módulo elástico y la tenacidad a la fractura de los materiales hasta 1000 °C “in situ” y (2) prueba para evaluar el comportamiento post-tratamiento térmico después de 2 horas de exposición a temperaturas que van desde 400 °C a 1000 °C. Los cambios mineralógicos y micro-estructurales que tienen lugar en los materiales se estudiaron por XRD, SEM/EDX y ^{27}Al y ^{29}Si MAS-NMR, DTA / TG. Los cambios en la distribución del tamaño de poro de las pastas cementantes también fueron estudiados por MIP después del calentamiento a temperaturas ≥ 600 °C. Los resultados obtenidos muestran que las pastas OPC perdieron totalmente la resistencia entre 400 y 600 °C, sin embargo, las pastas de HYC e HYP presentaron una mejor resistencia a altas temperaturas que las pastas cementantes OPC. La pasta FAN mostró buena resistencia residual después de su exposición al calor. Sin embargo, a temperaturas superiores a 800 °C, presenta un importante evento de contracción (especialmente en la prueba in situ) y grandes cambios en la porosidad, que se asoció con un proceso de sinterización parcial y la formación de nuevas fases minerales. Las diferentes fases formadas en los cementos en función de la temperatura de exposición se asocian con la diferente composición química de los cementos de partida y también con la diferente composición y microestructura del gel o geles mixtos que se formaron durante la hidratación. Los resultados obtenidos con los cuatro materiales cementantes estudiados pueden dar una idea general de la relación entre la composición elemental y el rendimiento a altas temperaturas. Será un factor importante a tener en cuenta al determinar el rendimiento a alta temperatura de futuros cementos y hormigones.

Resumiendo, los hallazgos de este trabajo mostraron que cementos con bajos contenidos en Clinker pueden ser manufacturarse industrialmente. Estos cementos con elevados contenidos de SCMs en presencia de un activador alcalino (sólido) presentan un desarrollo mecánico adecuado y pueden tener un mejor comportamiento a elevadas temperaturas que los cementos tradicionales de OPC.

Abstract

The main objective of this work is to study the effect of temperature on some specific cementitious binder materials with low clinker content and higher supplementary cementitious materials (SCMs) than blend cements. Those novel materials have been considered as one of potential solution to face environment issue caused by traditional cement industry especially CO₂ emission.

Specifically cements studied were: i) **OPC**: A commercial Portland cement Type *CEM I 42.5R* as reference; ii) **HYC**: pre-industrial hybrid alkaline cements contain 30 % of Portland cement clinker, 70 % mix of slag, fly ash and little solid activator (in design); iii) **HYP**: Pre-industrial cement: 50 % belite cement clinker and 50 % mix of fly ash and little solid activator (in design); iv) **FAN**: Alkali-activated fly ash binder (free clinker, activated by sodium hydroxide, as reference). Research has focused on the study of the effect of temperature on the early hydration process (in the pre-cure process), as well as on the effect of high temperature on hardened pastes (between 200 and 1000 °C).

First, it was studied how the curing temperature in the first 20 hours (25 ± 1 or $85 \text{ }^{\circ}\text{C}$) affects the initial hydration of these binder materials. The effect of the initial curing temperature on the hydration kinetics and the development of mechanical resistance at 2 and 28 days were explored. Its effect on the reaction products formed and the developed microstructure was also determined. The hydration products formed were characterized using XRD, SEM / EDX and ²⁷Al and ²⁹Si MAS-NMR. The results obtained showed that HYC and HYP when hydrated with water at room temperature ($25 \pm 1 \text{ }^{\circ}\text{C}$) set and harden reaching mechanical compressive strength values over 30 MPa, at 28 days. The main reaction product formed was a mix of cementitious gels: C-(A)-S-H and C-A-S-H for HYC and a mix of C-(A)-S-H, C-A-S-H and (N, C)-A-S-H for HYP. Curing at 85°C for 20 hours, they performed behaviour similar to OPC, inhibited ettringite formation and generated more polymerised gels, enhancing 3-day but not 28- or 90-day mechanical strength.

Secondly, with regard to the behaviour of the hardened pastes at high temperatures (from 200 to 1000 °C), two types of tests were carried out: (1) trial to determine the mechanical strength, the elastic modulus and the fracture toughness of materials up to 1000 °C “in situ” and (2) trial to evaluate post-thermal behaviour after two hours of exposure to temperatures ranging from 400 °C to 1000 °C. The mineralogical and micro-structural changes that take place in

the materials were studied by XRD, SEM/EDX and ^{27}Al and ^{29}Si MAS-NMR, DTA/TG. The changes in the pore size distribution of the cementing pastes were also studied by MIP after heating at temperatures $\geq 600^\circ\text{C}$. The OPC pastes totally lost the resistance between 400 and 600 $^\circ\text{C}$; however, the pastes of the HYC and HYP performed better high-temperature resistance than the OPC cementitious pastes. The FAN paste showed good residual strength after heat exposure. However, at temperatures above 800 $^\circ\text{C}$, it presents an important event of contraction (especially in the in situ test) and large changes in porosity, which was associated with a partial sintering process and the formation of new mineral phases. The different phases formed in the cements as a function of the exposure temperature are associated with the different chemical composition of the starting cements and also with the different composition and microstructure of the gel or mixed gels that were formed during hydration. The results obtained with the four cementitious materials studied can give a general idea of the relationship between elemental composition and high temperature performance. It will be an important factor to consider when determining the high temperature performance of future cement and concrete.

In summary, the findings of this work showed that cements with low Clinker content can be manufactured industrially. These cements with high contents of SCMs in the presence of an alkaline activator (solid) have a suitable mechanical development and can have a better behaviour at high temperatures than traditional OPC cements.

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1 State of the art

1.1 Portland cement

In the long history of coexistence and struggle between human and nature, it was an indisputable milestone that human started to move inside artificial building. The Greeks were, probably, the first to use lime-based cements as structural material. This technology was adopted and later improved by the Romans, who manufactured mortars with lime and sand. Then Romans engineers realized that when they finely milled certain volcanic deposits and mixed it with sand and lime, they got a product with higher mechanical strength and better resistance in both freshwater and saltwater. These volcanic deposits were called pozzolans (Massazza 1998).

Pozzolans are a siliceous materials that are not an intrinsically cement, but that combined with lime it originates a binder product with good properties.

Several centuries later, in the first half of the 18th, Portland cement was developed naturally from cements made in Britain (patented by Joseph Aspdin, in 1824). Its name is derived from similarity to Portland ITS stone, a type of building stone quarried on the Isle of Portland in Dorset of England. Further, in 1845, Isaac Johnson, refined the production of “meso-Portland cement” and used the mixture of clay and limestone as raw material. This is, claimed to be the real father of the actual Portland cement.

The most common use for Portland cement is in the production of concrete. Concrete is the most important composite material, especially as construction material. It consists of aggregate of gravel and sand, cement, and water. It can be cast in almost any shape desired, and once hardened, can become a structural element. Currently, Portland cement-based concrete is an excellent building material due to its mechanical strength properties and, good quality/price relation.

Portland cement is made by heating a mixture of limestone and clay, or other materials of similar bulk composition and sufficient reactivity, ultimately to a temperature of about 1450 °C. Partial fusion occurs, and nodules of clinker are produced. The clinker is mixed with a few per cent of calcium sulfate and finely ground, to make the cement (Jawed, Skalny et al. 1981, Neville 1995, H.F.W.Taylor (1997)). The clinker mainly has a composition with four types of oxides CaO, SiO₂, Al₂O₃, Fe₂O₃ and other fewer components, Na₂O, K₂O, MgO, SO₃..., which normally contains four crystalline phases, called alite, belite,

calcium aluminate and ferrite. Several other phases also present in minor amounts, such as alkali sulphates and calcium oxide and calcium sulphate.

Alite is the most important constituent of all normal Portland cement clinkers, of which it constitutes 50-60%. It is tricalcium silicate (Ca_3SiO_5) modified in composition and crystal structure by ionic substitutions. It reacts relatively quickly with water, and in normal Portland cements is the most important of the constituent phase for strength development; at age to twenty eight days, it is by far the most important. Belite constitutes 20-25 % of most normal Portland cement clinkers. It is dicalcium silicate (Ca_2SiO_4) modified by ionic substitutions and normally present wholly or largely as the β polymorph. It reacts slowly with water, thus contributing little to the strength during the first twenty eight days, but substantially to further increase in strength that occurs at large ages. By one year, the strength obtainable from pure alite and pure belite are about the same under comparable conditions. Calcium Aluminate constitutes 5-10 % of most normal Portland cement clinkers. It is tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$), substantially modified in composition and sometimes also in structure by ionic substitutions. It reacts rapidly with water, and can cause undesirably rapid setting unless a set-controlling agent, usually gypsum, is added. Ferrite makes up 3-10 % of normal Portland cement clinkers. It is tetracalcium aluminoferrite ($\text{Ca}_2\text{AlFeO}_5$), substantially modified in composition by variation in Al/Fe ratio and ionic substitutions. The rate at which it reacts with water appears to be somewhat variable, perhaps due to differences in composition or other characteristics, but in general is high initially and low or very low at large ages.

The general information of chemical composition and mineralogical composition of Portland cement clinker was presented in Table 1.1.1 (Sanz 2007).

Table 1.1.1 Chemical and mineralogical composition of Portland cement clinker

Chemical composition		Mineralogical composition	
Oxides	%	Phase	%
CaO	66-67	Alite: C_3S	50-60
SiO ₂	17-25	Belite: C_2S	20-25
Al ₂ O ₃	3.0-8.0	Aluminate: C_3A	5-10
Fe ₂ O ₃	0.5-6.0	Ferrite: C_4AF	3-10
MgO	0.5-4.0		
Me ₂ O (Me=K, Na)	0.3-1.2		
SO ₃	2.0-3.5		

1.1.1 Portland cement manufacturing process

Concrete has been used in the production of anything from civil structures to nuclear radiation shields, and from bridges to tunnels. The applications could be such widely variety because it can be poured into any shape. Cement is the substance material which holds concrete together, it means that it is extremely needed and used in our society.

How cement is made? From a popular science and industrial point of view, Portland cement (the only type of cement in common use today) is manufactured in a five step process:

- Quarrying
- Raw material preparation
- Clinker production (Firing of raw materials)
- Cement grinding
- Packing and Shipment

The main process of manufacture of Portland cement consists of three processes: raw material preparation, Clinker production and cement grinding.

1.1.1.1 Raw material preparation

The first step in the manufacture of Portland cement is to combine a variety of raw ingredients so that the resulting cement will have the desired chemical composition. These ingredients are ground into small particles to make them more reactive, blended together, and then the resulting raw mix is fed into a cement kiln which heats them to extremely high temperatures.

Since the final composition and properties of Portland cement are specified within rather strict bounds, it might be supposed that the requirements for the raw mix would be similarly strict. As it turns out, this is not the case. While it is important to have the correct proportions of calcium, silicon, aluminium, and iron, the overall chemical composition and structure of the individual raw ingredients can vary considerably. The reason for this is that at the very high temperatures in the kiln, many chemical components in the raw ingredients are burned off and replaced with oxygen from the air.

Grinding and blending prior to entering the kiln can be performed with the raw ingredients in the form of slurry (the wet process) or in dry form (the dry process). The addition of water facilitates grinding. However, the water must

then be removed by evaporation as the first step in the burning process, which requires additional energy. The wet process, which was once standard, has now been rendered obsolete by the development of efficient dry grinding equipment, and all modern cement plants use the dry process.

1.1.1.2 Clinker production

This is a step which is characteristic of Portland cement. A typical production process draft is given by Fig.1.1.1. The finely material is dried, heated and then cooled down again. During these processes, various chemical reactions take place to form the major mineral constituents of Portland cement. The powder from the dry process doesn't contain much moisture; it can be dried in a pre-heater tower and heated up to 800 °C. Then the mixture is then fed into the kiln. The slurry from the wet process contains more moisture to be successfully dried in a preheater tower. Instead, the slurry is fed directly into the kiln.

Figure 1.1.1 A typical clinker production process draft (XSM 2013)

The process of clinkering can be divided into varies steps depending on the temperature (H.F.W.Taylor 1997).

1. **Dehydration zone (up to ~ 450 °C):** This is simply the evaporation and removal of the free water. Even in the “dry process” there is some adsorbed moisture in the raw mix. Although the temperatures required to do this are not high, this requires significant time and energy. In the wet process, the

dehydration zone would require up to half the length of the kiln, while the dry process requires a somewhat shorter distance.

2. **Calcination zone (450 °C – 900 °C):** The term calcination refers to the process of decomposing a solid material so that one of its constituents is driven off as a gas. At about 600 °C the bound water is driven out of the clays, and by 900 °C the calcium carbonate is decomposed, releasing carbon dioxide. By the end of the calcination zone, the mix consists of oxides of the four main elements which are ready to undergo further reaction into cement minerals. Because calcination does not involve melting, the mix is still a free-flowing powder at this point.
3. **Solid-state reaction zone (900 °C- 1300 °C):** This zone slightly overlaps, and is sometimes included with, the calcination zone. As the temperature continues to increase above ~ 900 °C there is still no melting, but solid-state reactions begin to occur. CaO and reactive silica combine to form small crystals of C₂S (dicalcium silicate), one of the four main cement minerals. In addition, intermediate calcium aluminates and calcium ferrite compounds form. These play an important role in the clinkering process as fluxing agents, in that they molten at a relatively low temperature of ~ 1300 °C, allowing a significant increase in the rate of reaction. Without these fluxing agents, the formation of the calcium silicate cement minerals would be slow and difficult. In fact, the formation of fluxing agents is the primary reason that Portland (calcium silicate) cements contain aluminium and iron at all. The final aluminium- and iron-containing cement minerals (C₃A and C₄AF) in a Portland cement contribute little to the final properties. As the mix passes through solid-state reaction zone it becomes “sticky” due to the tendency for adjacent particles to fuse together.
4. **Clinkering zone (1300 °C – 1550 °C):** This is the hottest zone where the formation of the most important cement mineral, C₃S (alite), occurs. The zone begins as soon as the intermediate calcium aluminate and ferrite phases melt. The presence of the melt phase causes the mix to agglomerate into relatively large nodules about the size of marbles consisting of many small solid particles bound together by a thin layer of liquid. Inside the liquid phase, C₃S forms by reaction between C₂S crystals and CaO. Crystals of solid C₃S grow within the liquid, while crystals of belite formed earlier decrease in number but grow in size. The clinkering process is complete when all of silica is in the C₃S and C₂S crystals and the amount of free lime (CaO) is reduced to a minimal level (< 1 %).

5. **Cooling zone:** As the clinker moves past the bottom of the kiln the temperature drops rapidly and the liquid phase solidifies, forming the other two cement minerals C_3A (aluminate) and C_4AF (ferrite). In addition, alkalis (primarily K) and sulphate dissolved in the liquid combine to form K_2SO_4 and Na_2SO_4 . The nodules formed in the clinkering zone are now hard, and the resulting product is called cement clinker. The rate of cooling from the maximum temperature down to about 1100 °C is important. It affects the way in which the belite transitions occur as well the alite crystal size, rapid cooling giving smaller crystals and more reactive cement. If the clinker is cooled slowly in the region from 1250 °C to about 1100 °C, the C_3S begins to decompose. An intimate mixture of belite and lime forms pseudomorphs after alite and the decomposition is especially likely to occur if the clinker has been fired under reducing conditions. It is thus typical to blow air or spray water onto the clinker to cool it more rapidly as it exits the kiln.

1.1.1.3 Cement grinding

Once the nodules of cement clinker have cooled, they are ground back into a fine powder in a large grinding mill. At the same time, a small amount of calcium sulphate such as gypsum (calcium sulphate dehydrate) is blended into the cement. At this point the manufacturing process is complete and the cement is ready to be bagged or transported in bulk away from the plant.

1.1.2 Hydration of Portland cement

Hydration absolutely depends on cementitious materials. It is the, almost magical, process by which suspension is transformed into a rigid solid, at room temperature, without the need for heat or other external processing agents and with minimal bulk volume change.

Then hydration process is associated with a sequence of chemical reactions between the phases of the clinker, calcium sulphate and water. First set and then harden. The main processes taking places in the hydration of Portland cements (PC) are well known. The clinker phases hydrate at various rates resulting mainly in the formation of C-S-H, Portlandite, ettringite and AFm phase (H.F.W.Taylor 1997).

The hydration speed of the phased which consist of clinker is different. In general, aluminates phase reacts very quickly and belite phase reacts most slowly, the reaction velocities among the phases are shown as following:

The main reactions during the hydration phases are listed in the Table 1.1.2

Table 1.1.2 The main hydration reactions in phases of Portland cement (Bosque 2012).

C₃S	$2 C_3S + 7H \rightarrow C_3S_2H_4 \text{ (gel C-S-H)} + 3CH$
C₂S	$2 C_2S + 5H \rightarrow C_3S_2H_4 \text{ (gel C-S-H)} + CH$
C₃A	<p>In the absence of calcium sulfate (very quick)</p> $2C_3A + 27 H \rightarrow C_4AH_{19} + C_2AH_8$ $2C_3A + 21 H \rightarrow C_4AH_{13} + C_2AH_8$ $C_4AH_{19} + C_2AH_8 \rightarrow 2 C_3AH_6 + 15H$ <p>In the presence of sulfate</p> $C_3A + 3 \bar{C}SH_2 + 26 H \rightarrow C_6\bar{A}\bar{S}_3H_{32} \text{ (ettringite)}$ $2C_3A + C_6\bar{A}\bar{S}_3H_{32} + (n - 8) H \rightarrow 3 C_4\bar{A}\bar{S}H_{12} \text{ (} n = 12 - 14 \text{)}$
C₄AF	$C_4AF + 3 \bar{C}SH_2 + 30 H \rightarrow C_6\bar{A}\bar{S}_3H_{32} + \{FH_3\}^* + CH$ $C_4AF + 6 \bar{C}SH_2 + 2 CH + 50 H \rightarrow C_6AF(\bar{C}\bar{S})_6H_{64}$ $2 C_4AF + C_6\bar{A}\bar{S}_3H_{32} + 12 H \rightarrow 3 C_4\bar{A}\bar{S}H_{12} + 2 \{FH_3\} + 2 CH$ $2 C_4AF + 2 C_6\bar{A}\bar{S}_3H_{32} + 4 CH + 4 H \rightarrow 2 C_9A_2F(\bar{C}\bar{S})_3H_{36}$

* FH₃ is not a specific composite

The hydration process of Portland cement can be studied by isothermal conduction calorimetry. According to the calorimetry curve of heat flows, the hydration process of Portland cement can be divided into five stages: 1) pre-induction period; 2) induction period; 3) acceleration period; 4) deceleration period; 5) diffusion period (see Fig.1.1.2).

Figure 1.1.2 Heat evolution and process during the hydration of Portland cement.

When the cement contacts with water, an exchange of ionic species takes place between the solid and the liquid phase, which results in a rapid increase concentration of aluminates, sulphates and alkalis in the liquid phase. During this period (pre-induction), a large amount of heat evolution appeared and primary ettringite are formed. The Ca^{2+} and Si^{4+} ions from the C_3S start the dissolution and pass into solution, the silica concentration reaches a maximum and then decreases rapidly, the calcium still increases.

In the induction period, the dissolution continues, and the concentration of calcium and OH^- increases. At this stage, the heat evolution rate drops and the concentration of Ca^{2+} ions in the liquid phase reaches supersaturation, thereby it initiates the nucleation of C-S-H gel and starts the precipitation of portlandite.

During the induction /acceleration period, a layer of gel C-S-H and ettringite has been formed coats around clinker particles, which decrease the concentration of Ca^{2+} ions in the liquid phase. As a result of low concentration of Ca^{2+} , the dissolution rate of C_3S and heat evolution increase. At stage of acceleration, the main C_3S hydration starts and the continuous precipitation of reaction products, gel C-S-H and portlandite occurs.

The deceleration period of hydration process is characterized by a low heat evolution and slow reaction rates. In this stage, the deceleration is due to chemical reactions which are controlled by diffusion processes and precipitation of reaction products (Jawed, Skalny et al. 1981, Neville 1995). Further aluminate, C_3A , hydration happened in this stage. In Portland cement, this phase also

affects the hydration kinetics in the first few days. In the Table 1.1.2, the hydration of C_3A with and without calcium sulphate was listed. The reaction is very quick, whose quick setting behaviour is undesirable in concrete. For retarding the fast reaction of C_3A , calcium sulphate is added to Portland cements to control the reaction (Minard, Garrault et al. 2007).

Fig.1.1.3 exhibited a typical shoulder peak where a secondary formation of ettringite occurs and subsequent broad peak (about 20 h and 30 h) corresponding to the formation of AFm phase(s) which is shorthand for a family of hydrated calcium aluminate phases (Matschei, Lothenbach et al. 2007). A representative formula is $[Ca_2(Al, Fe)(OH)_6] \cdot xH_2O$ where X equals an exchangeable singly charged (e.g. chloride) or half of a doubly charged anion (e.g. sulphate, carbonate and aluminosilicate).

Figure 1.1.3 Calorimetry curve of modern Portland cement (Bullard, Jennings et al. 2011).

A recent study by Bazzoni et al. (Bazzoni 2014) proposed that the growth of C-S-H “needles” controlled the main heat evolution peak. This theory considered that the needles nucleate on the surface of grains and, those correctly oriented, grow outwards. There appears to be certain length, before the needles grow fast and then the growth became slowly. With the needles nucleating and growing, the surface of the grains is covered until it is impossible for C-S-H gel to grow in this manner. The mechanism is described in Fig.1.1.4. It mainly happened in the stage of acceleration and deceleration.

Figure 1.1.4 Schematic of relationship between main heat evolution peak and growth of C-S-H “needles” (Bazzoni 2014).

1.1.3 The structure of gel C-S-H

The main reaction product in the hydration of Portland cement is a gel, named hydrated calcium silicate, which is rapidly formed from the hydration of alite and more slowly from the belite hydration. The calcium silicate hydrate (C-S-H gel) is the one that gives the cement its tough and durable properties. It's an amorphous compound with a Ca/Si ratio varies with hydration time and conditions. Structurally speaking, this product is formed by silicon tetrahedrons which linked together to form linear chains of 2, 5, 8 ... $(3n-1)$ links. The chain length increases with the time of hydration. There are two models to describe the structure of gel C-S-H. Both models considered that the C-S-H gel has a structure of disordered layers.

- Model proposed by Tylor (Taylor 1986, Taylor 1993)
- Model proposed by Richardson and Andersen (Richardson and Groves 1993, Richardson 2004).

Fig. 1.1.5 showed the structural model proposed by Taylor for the gel C-S-H. In this model it is noted that many of the layers are disordered. It is structurally similar to imperfect Jennite layer and the other, is similar to the 1.4 nm tobermorite layers. In this structure, silicates chain are "dreierketten", the structure is repeated at intervals of three tetrahedrons.

In 1.4 nm tobermorite layer, each interval tetrahedral shares two oxygen atoms with two core sheet Ca-O tetrahedron while the third one is not join to the central sheet. The data obtained by the NMR spectra confirmed that in this

structure, type tobermorite, the long chain is predominant of the units Q^2 . However Jennite layer is formed by short chains and distorted tetrahedron, each short chain can tilt, rotate or move. Many tetrahedra bridges have disappeared, the dimers in this structure result in the units Q^1 became predominate.

On the other hand, Richardson et al. proposed a model of gel C-S-H. It is similar to the Taylor's model, which assumed that the aluminum may replace silicon in the tetrahedrons bridge site. This incorporation of aluminum in the C-S-H phases can be detected by ^{29}Si or ^{27}Al MAS NMR. The signal related to this position was detected at -82 ppm assigned to the units Q^2 (1Al). The charge balance was made possible by the addition of alkali cations of the Ca^{2+} between the layers. This model was represented by Andersen (Andersen, Jakobsen et al. 2004), which showed that the chain SiO_4 tetrahedral was in the top of Fig.1.1.6. It is a metamer unit where two tetrahedra SiO_4 bridge (Q^2_B) joining three dimers, which resulted in two groups SiO_4 chain end (Q^1) and four groups SiO_4 (Q^2_P). In addition, a defect was shown in the structure of tobermorite there the bridge disappeared, which gives rise to two neighboring sites Q^1 .

Figure 1.1.5 The model of C-S-H structure, redraw from (Taylor 1992).

Figure 1.1.6 The model of C-S-H (Andersen, Jakobsen et al. 2004).

1.2 The eco-environment issues of cement industry

It is world widely accepted that global warming is indeed the major environmental and economic threat in our planet. The global warming is caused by the emissions of greenhouse gases (GHGs) related to human activities. Rapid industrial extension and dramatic increase of public individual transportation have been lead to GHGs (Progressive Emissions of Greenhouse Gases) (Benhelal, Zahedi et al. 2013), which already reaches to an alarming level. As we known, this accumulation will result in increase of global mean temperature (GMT) in 21st century if we don't control and mitigate. There is expecting catastrophic events related to the increase in GMT, which listed below in Table 1.2.1.

Cement production is responsible for almost 7-10 percent of human greenhouse gases (GHG), specifically CO₂ emissions. Nevertheless, cement still remains the key materials to satisfy global housing and modern infrastructure needs, it is one of the most used today. Therefore, the eco-environment issues around cement industry have become significant and imminent global topic not only for cement industry but also for cement scientific researchers.

Table 1.2.1 The global risks due to increase in GMT.

Systems problem	Smith <i>et al.</i> (Realff, Lemieux <i>et al.</i> 2005) reported that 20-30% of known plants and animals would extinct because of the increase in GMT above 1990 levels by 1-2.5 °C, which poses risks to many unique and threatened systems, including many biodiversity hotspots.
Weather events	Climate change (Parry 2007) announced that the increase in heat waves, intense precipitation events, and the intensity of tropical cyclones are amongst the extreme weather events which will happen if GMT continuously rises up.
Large-scale discontinuity	Climate change (Solomon 2007) and Rahman <i>et al.</i> (Smith, Schneider <i>et al.</i> 2009) reported that global warming over many centuries would lead to a sea level rise which is associated to loss of coastal area and other impacts

1.2.1 Greenhouse emissions (CO₂) from cement industry

The cement industries contributed for about 7 % of global CO₂ emissions according to the report by J. Deja *et al.* (Deja, Uliasz-Bochenczyk *et al.* 2010). Emissions of CO₂ in a cement industry mainly come directly from combustion of fossil fuels and from calcinations of the limestone into calcium oxide. An indirect amount of CO₂ comes from the consumption of electricity that is generated by burning fossil fuels. Approximately half of CO₂ emissions are originated from the combustion of fuels and half of them are originated from the calcinations of the limestone (Ali, Saidur *et al.* 2011).

According to the report (Intergovernmental Panel on Climate 2015), industrial CO₂ emissions were 13.14 GtCO₂ in 2010. CO₂ emissions from only cement-forming reactions were 1.34 GtCO₂. From 1990 to 2010, cement production (for statistical reasons ‘Cement production’ only covers process CO₂ emissions) contributed 7.2 % up to 13% in total global industry and waste/wastewater direct GHG emissions (see Fig. 1.2.1).

Figure 1.2.1 Total global industry and waste/wastewater direct GHG emissions by region, 1970–2010 (GtCO₂ eq/yr) (Intergovernmental Panel on Climate 2015).

CO₂ emission from calcination: Almost half of the CO₂ is produced from the calcination process where conversion of raw materials takes place (Deja, Uliasz-Bochenczyk et al. 2010). The calcination process depends largely on clinker production according to the fact that all of the CaO and MeO in the clinker are produced from a carbonate source. The amount of CO₂ generated by the process varies on the basis of loss of the raw materials (limestone) during ignition. Fig. 1.2.2 shows the mass balance results of CO₂ emissions in a cement manufacturing process.

Figure 1.2.2 Typical cement process mass balance (Ali, Saidur et al. 2011).

CO₂ emission relating to the cement manufacturing process: the Fig.1.2.3 exhibited schematically the cement production process and associated CO₂

emissions at different sections of a cement manufacturing process, which was introduced in chapter 1.1.1 before. The major raw material used in producing cement is limestone. Emissions are produced mainly by de-carbonation of limestone and the use of carbon based fuels for heating. During cement production process, around 0.92 t of CO_2 is released for each ton of clinker produced which mainly come from de-carbonation of limestone (0.53 t) and the use of carbon-based fuels for heating (0.39 t) (Gartner 2004). Nearly 0.1 t of CO_2 emissions (average) per ton of cement are associated with grinding processes mostly related to electricity production.

Figure 1.2.3 Simplified cement fabrication process, with a specific interest in the CO_2 emissions (Habert, Billard et al. 2010).

1.2.2 Brief data report of cement industry

The world cement production in 2015 was shown in Fig. 1.2.4. China still is the first country that produces more than half of cement in the world. It is pertinent that many of the large cement industries are now in developing country. With the development needs of urbanization and infrastructure, cement demand is forecasted to be growing in future.

Fig. 1.2.5 shows global cement production increasing constantly from 1990 to 2050 (Imbabi, Carrigan et al. 2012). This is to be expected as it is the main

consumed product on the planet in decade's years. The industry is growing especially rapidly in developing countries such as India and in China. In these countries, they have a high demand for infrastructure and housing.

Figure 1.2.4 World cement production by region and main countries (%) (CMBUREAU 2015).

Figure 1.2.5 World Portland cement production 1990-2050.

1.2.3 The challenge for cement industry

Nowadays sustainable development of human being has become the most important topic in all walks of life, especially in the field of industry and energy. The cement industry in general has assumed two important challenges for environment. The first is to reduce particle and gas emission, the second is to reduce greenhouse gas (CO₂) emission.

On the other hand, the durability problems inherent in Portland cement concrete have been never stopped to debate. Around 20-25% of the Portland cement fabricated yearly all over the world is used to repair structures in service (Palomo, Krivenko et al. 2014).

External (environment and energy) and internal (durability) interaction promote the development of cement industry. In cement, the reduction of clinker factor remains a key priority according to the fact that clinker production consumes more energy and raw material and at the same time generates more particle, gas and greenhouses gas emission. Nevertheless, appropriate materials are limited in their regional availability. Tremendous progress has already been made. In the future, new material might be playing a role as cement constituents to produce more sustainable cement.

In any case, it should be clearly aware of the fact that immediate global replace of Portland cement by any other type of cement or binder materials is virtually impossible. Scientific community and cement manufacturers know this problem and have been working on the possible alternatives for many years. Some of these new materials are discussed below:

Belite cements: One solution is the partial substitution of the high-lime cement by the lower temperature belite phase with the stabilization of the more active belite polymorph, the α' -phase (Chatterjee 1996). Belite (di-calcium silicate, C₂S) based cement has been proposed as environmentally friendly building materials due to their production may release up to 35 % less CO₂ in to the atmosphere when comparing to OPC (Martín-Sedeño, Cuberos et al. 2010). This reduction of energy attributes to 1) less limestone in the raw feed; 2) a lower burning-zone temperature, (1250 °C, as opposed to 1450 °C for OPC) and 3) each of cement grinding due to clinker porosity (Quillin 2001). The main disadvantage of the belite cements is that the rate of hydration of C₂S is very slow with respect to C₃S (alite), and therefore the initial mechanical strengths of the belite cements are low. Intensive research on belite-based cement has been conducted for

decade's worldwide (Sui, Fan et al. 2015). The development of reactive belite based Portland cement in China since 1996 and its application in the world largest hydropower project and the Three Gorges Dam project demonstrate that HBC (high belite cement) is not only a kind of low energy and low E (low emission) cement, but a better solution for high performance concrete making. The revival of research on BCSA (belite based calcium sulfoaluminate) cement in the world is another example of exploring the low E clinker new binder towards cement and concrete sustainability issues (Gartner and Quillin 2007).

Blended cement or pozzolanic cements: Nowadays it is the most considered option, it is to dilute Portland clinker content in the cement with other materials of lower energy consumption and less CO₂ emission. The use of supplementary cementitious materials (SCMs) as addition to OPC, where no additional clinkering process is involved, results in the reduction in CO₂ emissions. It is because the most energy consuming stage in the cement industry is the clinkering process as mentioned before. Normally the SCMs used are: pozzolanic clay, metakaolin, coal fly ash and blast furnace slag (Malhotra and Mehta 1996). In fact this technology is widely used today by most cement factories. Building codes the world over specify both the type and maximum amount of additions that cements can bear (see EN-197-1(197-1:2011 2011), cement Type II, III, IV and V). New research in this area goes in the direction of how to improve the reactivity of SCMs (Lothenbach, Scrivener et al. 2011) and the possibility to use other materials as SCMs especially waste form the industry.

Alkaline cements. A relatively new option is to make Clinker-free cementitious materials, known as alkali-activated binders, also called geopolymers. This cement has been studied over the last old decades. The major differences between the alkali-activated based cement and OPC are; they don't have clinker and they are mixed with highly alkaline chemicals not with water (Fernández-Jiménez and Palomo 2005, Duxson, Fernández-Jiménez et al. 2007). In some cases, special curing conditions are required, such as alkali-activated fly ash (60 °C to 90 °C curing temperature). Due to the relative novelty of these cements, a little review of the performance will be doing in section 1.3.

Hybrid or blended alkaline cements: These cements are relatively new and are the outcome of combining the existing knowledge of OPC and alkaline cements (Palomo, Fernández-Jiménez et al. 2007, García-Lodeiro, Fernández-Jiménez et al. 2013, Garcia-Lodeiro, Fernandez-Jimenez et al. 2013, Palomo, Krivenko et al. 2014) typically contain a low Portland cement ($\leq 30\%$) and a high content of supplementary cementitious materials ($\geq 70\%$), along with a small proportion of

an alkaline activator to favour initial strength development ([Palomo, Fernández-Jiménez et al. 2007](#), [Garcia-Lodeiro, Fernandez-Jimenez et al. 2013](#), [Donatello, Maltseva et al. 2014](#)) Also these cements will be explained with more details in section 1.3.

In this thesis have been considered the different possibility previously indicates to obtain sustainable cements, as will be indicated in the objective of this thesis (chapter 2) and in chapters 4 and 5. In particular the cements studied have been:

- OPC: A commercial Portland cement Type *CEM I 42.5* as reference
- HYC: pre-industrial hybrid alkaline cements contain 30 % of Portland cement clinker, 70 % mix of slag, fly ash and little solid activator (in design, details in chapter 4).
- HYP: 50 % Belite cement clinker and 50 % mix of fly ash and little solid activator (in design details in chapter 4).
- FAN: Alkali-activated fly ash binder.

1.3 A review of alkaline activation technology

According to the new book about alkali-activated cements, mortars and concretes which has been published in 2015, In general, alkaline cements are group of cementitious materials formed as the result of an alkaline attack on the amorphous or vitreous aluminosilicates. When mixed with alkaline activators, these materials set and harden, yielding a material with good binding properties ([Pacheco-Torgal, Labrincha et al. 2014](#)).

Dating back to 1930, Kühl studied the setting behaviour of mixtures of slag ground to a powder and a KOH solution and first time to use the alkalis as a component of cementitious materials. Since that time many researchers have been done on the role that alkali may play in potential cementitious system. A brief bibliography listing of some important events in the history of alkali activated cement was shown by Table 1.3.1.

In the last few decades, many studies on alkaline activation have been conducted. A very wide range of natural raw materials, industrial by-products and recycled aluminosilicates can be used as alkaline cement components: metakaolin, pozzolans, blast furnace slag, phosphorous slag, fly ash, glass waste and combinations of two or more of these materials ([Shi, Jiménez et al. 2011](#)).

Table 1.3.1 Alkali Activated cements timeline (Palomo, Krivenko et al. 2014).

Year	Name	Study / Impact
1930	Kühl	Slag setting in the presence of dry potash
1937	Chassevent	Slag reactivity measurement using a dry potash and soda solution
1940	Purdon	Clinker-free cements consisting of slag and caustic soda or slag and caustic alkalis synthesized with a base and an alkaline salt
1957	Glukhovsky	Binder synthesis using hydrous and anhydrous aluminosilicates (vitreous rocks, clays, steel mill slag) and alkalis; proposal for a $\text{Me}_2\text{-MeO-Me}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ cementitious system; coining of the term “soil cement”.
1981	Davidovits	Alkalis mixed with a blend of burnt kaolinite, limestone and dolomite, and trademarks such as Geopolymer, Pyrament, Geopolycem, Geopolymite.
1986	Krivenko	Principles governing system $\text{Me}_2\text{-MeO-Me}_2\text{O}_3\text{-SiO}_2\text{-Al}_2\text{O}_3$ properties; proposal for the generic name “alkaline cements” and the specific name “geocement”.
1999	Palomo	Production of hardened cementitious materials from alkali-activated type F fly ashes.
2006	Shi&Krivenko&Roy	First book on alkali-activated cements.
2014	Provis J, & Van Deventer J.S.J	Alkali activated materials state of the art Report. RILEM TC 224-AAM.
2015	Pacheco-Torgal, F. Labrincha, J. A. Leonelli, C. Palomo, A. Chindapasirt, P.	Handbook of Alkali-Activated Cements, Mortars and Concretes

Although the characteristics of the raw materials and processing conditions play significant roles in the hydration procedure and microstructural development of the binders, with the concomitant variations in their mechanical strength, alkali-cements and concretes could exhibit in some cases a higher performance than Portland cement concretes (Davidovits 1994).

To demonstrate the nature of the raw materials affects the progress and development of chemical reactions, it is made then a simultaneous discussion of the differences that characterize materials based on blast furnace slag and fly ash based.

Based on the nature of their chemical composition (CaO-SiO₂-Al₂O₃ system), alkaline cements can be grouped under different categories

Group 1, High calcium content: (Na,K)₂O-CaO-Al₂O₃-SiO₂-H₂O system, model 1

In this group, calcium and silicon-rich materials such as blast furnace slag (SiO₂+CaO > 70%) can be activated under relatively moderate alkaline conditions at around curing temperature 20 °C (Bakharev, Sanjayan et al. 2000, Fernández Jiménez 2000, Shi, Roy et al. 2006). The main reaction product formed is kind of calcium silicate hydrate gel, C-A-S-H. It is quite similar to the gel obtained during Portland cement hydration, which take up Al in this structure.

Group 2, Low calcium content: (Na,K)₂O-Al₂O₃-SiO₂-H₂O system, model 2

In this group, aluminum and silicon are comprised primarily the activated materials. These materials are of type: metakaolin or fly ash type F (according to the ASTM classification, from coal-fired steam plant), which have low calcium contents. For this kind of material, the alkaline activation required more aggressive working conditions, normally highly alkaline media and high curing temperature (60-200 °C), than group one. The main reaction product formed is a three-dimensional inorganic alkaline polymer, which defined as alkaline aluminosilicate hydrate gel, called N-A-S-H gel among reference. This kind of gel can be regarded as a zeolite precursor (Palomo, Grutzeck et al. 1999, Palomo, Alonso et al. 2004, Fernández-Jiménez and Palomo 2005, Duxson, Fernández-Jiménez et al. 2007, Provis and Van Deventer 2009). This group is also generically called a “geopolymer” or an “alkaline inorganic polymer”. Although there is conceptual confusion among different researchers, most of the scientific communities apply the same technology. In any case, these terms are only used to describe this group of materials.

Group 3, Hybrid alkaline cement, Model 3

Today, a third alkaline activation model, a combination of the preceding two, also be described (Palomo, Krivenko et al. 2014). Hybrid alkaline cement is a new type of binder, formed as the result of the alkaline activation of materials with CaO, SiO₂ and Al₂O₃ contents > 20 % (Alonso and Palomo 2001, Yip, Lukey et al. 2005). The activation procedure could be described as the third

model. Typically, these binders contain low Portland cement clinker content (< 30 %) and high proportion (> 70 %) of mineral additions, which normally are aluminosilicate materials (ASMs), such as fly ash, slag, fly ash + slag. The content of aluminosilicate materials is significantly higher than it in blended pozzolanic cements. These cements can also be regarded to lie in an intermediate position on the OPC / alkaline cements spectrum, as illustrated in Fig.1.3.1. Curing condition, such as curing temperature and activator selection, play an important role in the behaviour of hybrid alkaline cement. The reaction products precipitating as a result of hybrid cement hydration are complex. It has been studied in recent years (Alonso and Palomo 2001, Yip, Lukey et al. 2005, Palomo, Fernández-Jiménez et al. 2007, García-Lodeiro, Fernández-Jiménez et al. 2013) and described as a mix of cementitious gels, including C-A-S-H (containing sodium) and (N, C)-A-S-H (high calcium content N-A-S-H gels) gels.

Figure 1.3.1 Position of hybrid alkaline cements on the pure Portland cement (PC)-pure alkaline cement spectrum, relative to pozzolanic blended cements. ASMs* is aluminosilicate materials.

While much research has been done on the materials of OPC, blended cements and alkaline cements with many years, relatively speaking, not much has been published in hybrid alkaline cements.

One advantage factor that OPC has been used as an excellent binder material in construction industry is the easy hydration condition, such as it can hydrate at room temperature and with water. On the other hand, one of the arguments against the use of pure alkaline cements have centred on practical health and safety issues around the preparation and storage of highly alkaline solutions on construction factory sites. One attempts made to surmount this contradiction is the use of hybrid alkaline cements which need moderate alkaline solutions and normal temperature to hydrate.

1.3.1 Alkaline activation reaction in calcium-rich systems: Group 1.

The most useful material to prepare calcium-rich alkaline cements and concretes is blast furnace slag. It is a vitreous product formed as the result of the combination of acid oxides (SiO_2 and Al_2O_3) from the mix of acid clay gangue present in iron ore and sulphur ash in coke with the basic oxides (CaO and MgO) in the limestone or dolomite used as fluxes smelted at high temperature (1600°C) and then abruptly cooled to temperature of around 800°C (Fernández Jiménez 2000, Shi, Roy et al. 2006).

Numbers of research have been studied for the reactivity of slag in alkaline activation processes. It has been agreed that the reactivity depends largely on (Swamy and Bouikni 1990, Mostafa, El-Hemaly et al. 2001, Li, Xu et al. 2002):

- The component phase of slag
- The vitreous structure of slag

Some authors (Swamy and Bouikni 1990) recommended that the vitreous phase content should be over 90%. However, S.C. S.C. Pal *et al.* (Pal, Mukherjee et al. 2003) reported that low vitreous phase contents (30-60%) could also perform good results. A consensus of the degree of depolymerisation (DP) parameter, which the value apparently relates to slag reactivity was made by researchers (Pal, Mukherjee et al. 2003, Provis and Van Deventer 2009, Li, Sun et al. 2010). It is calculated from the equation 1.2.1

$$\text{DP} = [\text{n}(\text{CaO}) - 2\text{n}(\text{MgO}) - \text{n}(\text{Al}_2\text{O}_3) - \text{n}(\text{SO}_3)] / [\text{n}(\text{SiO}_2) - 2\text{n}(\text{MgO}) - 0.5\text{n}(\text{Al}_2\text{O}_3)] \quad (1.2.1)$$

A. Fernández-Jiménez (Fernández-Jiménez and Palomo 2003) reported that the nature of the anion in the solution also plays an instrumental role in alkaline activation, especially in the early stages of hydration and in particular with regard to paste setting. Their model for the reaction mechanisms (based on a

model proposed by Glasser in 1990 is shown in Fig.1.3.2 (Palomo, Krivenko et al. 2014).

Figure 1.3.2 Reaction mechanism in alkali-activated slag particle (Adapted).

1.3.1.1 Reaction products

The most important product formed in Portland cement hydration aforementioned is a C-S-H like gel. The material primarily owes its mechanical properties to this gel. Portlandite, ettingite and calcium monosulfoaluminate was formed as secondary products (H.F.W.Taylor 1997). In alkaline cements based on the materials with high calcium content such as blast furnace slag, the reaction products are resemble to the products precipitated during Portland cement hydration. The main reaction product formed during alkaline activation is a C-A-S-H like gel. Comparing with the typical C-S-H gel formed from Portland cement, the gel has a lower Ca/Si ratio, 0.8-1.2 and different structure. The secondary products normally include hydrotalcite, calcite and bases such as AFm, which largely depend on the starting material composition, activator, curing condition and pH.

I. Garcia-Lodeiro et al. (Garcia-Lodeiro, Palomo et al. 2015) has summarized the reaction products forming during alkaline activation of materials as following:

- The main hydration product is a calcium silicate hydrate taking with aluminium into its composition, which called C-A-S-H. The gel has a slightly distinguish with the gel produced in Portland cement paste because of its lower Ca/Si ratio.
- The minority phases formatted during the alkaline activation of slag which found by some authors have reached a broad consensus.

- (1) Hydrotalcite - $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$, This phase has been detected in slag activated with NaOH (Fernández-Jiménez and Palomo 2003, Haha, Lothenbach et al. 2011, Haha, Lothenbach et al. 2012) and waterglass (Qing-Hua, Tagnit-Hamou et al. 1991, Wang, Pu et al. 1995). Hydrotalcite is a natural mineral whose structure consists of layers of brucite ($\text{Mg}(\text{OH})$) with interstitial water molecules and CO_3^{2-} ions.
- (2) C_4AH_{13} -type phases have been detected in slag activated with NaOH. These phases form platelets 0.1-0.2 μm thick and approximately 1.5 μm diameter (Wang, Pu et al. 1995). Other carbonated phases such as $\text{C}_4\text{A}\bar{\text{C}}\text{H}_{11}$ and $\text{C}_8\text{A}\bar{\text{C}}_2\text{H}_{24}$ have been observed by other authors (Qing-Hua, Tagnit-Hamou et al. 1991) in slag pastes activated with NaOH and $\text{Ca}(\text{OH})_2$.

1.3.1.2 Structure of gel formed: C-A-S-H

Many researches (Roy, Schilling et al. 1992, Wang, Pu et al. 1995, Cong and Kirkpatrick 1996, Richardson and Groves 1997, Fernández-Jiménez, Puertas et al. 2003, Haha, Lothenbach et al. 2011) on the microstructural development during alkaline activation of slag-based material have been made by different techniques.

In the Fig.1.3.3, it reproduced the micrographs of the initial slag and its alkaline activation products hydrated with two alkaline activator, NaOH and waterglass (Fernández-Jiménez, Puertas et al. 2003). This study used transmission electron microscopy (TEM) to confirm that the main reaction product is a foil-like semi-crystalline calcium silicate hydrate.

The nanostructure of cementitious gels cannot be clearly detected and determined by the additional technique because of the amorphous nature. With the development of a numbers of characterization techniques, especially after the application of nuclear magnetic resonance (NMR), the models have been helpfully developed used to ascertain and describe the structure.

As previously mentioned, the model for the C-S-H formed during OPC hydration is based on the structure of defective tobermorite, also called dreierkette-type chains (Taylor 1986, Cong and Kirkpatrick 1996). Perfect tobermorite consists of two linear chains of silica tetrahedral arranged on either side of a central sheet of CaO. The linear chains consists of a repetitive series of three terahedra, two of which are connected to the centre sheet of CaO with two

oxygen bridge and the third, known as bridging tetrahedron, is not. In the nanostructure of C-S-H gel, many of the bridging tetrahedra are missing, which give rise to two-, three-, or five-link chains. Basing on ^{29}Si and ^{27}Al MAS NMR studies, Schilling and his group (Schilling, Butler et al. 1994) proposed that in alkali-activated slag pastes Al is taken up in the C-S-H gel. In the structure, aluminium tetrahedra replace silicon tetrahedra in bridging positions to give rise to Q^1 , Q^2 and Q^3 (1Al) units. The aluminium uptake was studied to be influenced by the concentration of alkalis and curing temperature and humidity.

Figure 1.3.3 TEM micrographs of (a) anhydrous slag ($\text{Ca/Si} = 1.21$, $\text{Ca/Al} = 2.63$, $\text{Si/Al} = 2.13$); (b) slag hydrated with NaOH for 7 days ($\text{Ca/Si} = 0.93$, $\text{Ca/Al} = 1.35$, $\text{Si/Al} = 1.45$); (c) slag hydrated with waterglass for 7 days ($\text{Ca/Si} = 0.64$, $\text{Ca/Al} = 1.49$, $\text{Si/Al} = 2.32$) (Fernández-Jiménez, Puertas et al. 2003).

The model was subsequently ratified by Fernández-Jiménez et al. (2000.2003). They confirmed that the presence of Al gives rise to gels with longer linear chains as well as to the possible existence of sporadic inter-chains, Si-O-Al bonds and consequently two-dimensional ($\text{Q}^3(\text{mAl})$) unit, cross-linked) structures. In the Fig.1.3.4 we can see that, under that condition, the C-S-H gel would become C-A-S-H gels.

The type of activator has a significant effect on the gel structure. When the activator used was waterglass, highly condensed structure formed. Consequently, a substantial number of Q^2 (1Al) and Q^3 (mAl) units were observed, along with Q^1 (0Al) and Q^2 (0Al) units, favoring the formation of two-dimensional, cross-linked structures. When NaOH was the activator, however, the C-(A)-S-H generated had a significant number of Q^2 (1Al) units, but no Q^3 unit (Fernández-Jiménez, Puertas et al. 2003). In a recent article (Puertas, Palacios et al. 2011), reported that in C-A-S-H gels forming in slag activated with a NaOH solution, the existence of tetrahedral Al in bridging positions in the silicate chains goes

hand-in-hand with a considerable increase in the number of Q^2 (1Al) units, as well as with a small amount of Q^3 (mAl) units. When waterglass was used as an activator, higher aluminium content was observed in tetrahedral bridging positions of C-A-S-H gels formed, which favored chain cross-linking and raised the percentage of Q^3 (mAl) units dramatically and with it the formation of layered structures in certain regions.

Figure 1.3.4 Structural model for an Al-containing C-S-H gel; (a) linear chains ;(b) linear chains with occasional cross-linking, forming planes C-A-S-H gel (Fernández Jiménez 2000, Fernández-Jiménez, Puertas et al. 2003).

1.3.2 Alkaline activation in low-calcium systems: Group 2.

In alkaline activation of low-calcium systems, the most commonly materials used in alkaline cement and concrete are fly ash and metakaolin. Comparing with high cost of metakaolin, fly ash now is used widely as supplementary material in the cement industry.

Fly ash is an industrial by-products coming from coal-fired steam power plants, where the coal is ground to a fine powder before being used as a fuel (Palomo, Krivenko et al. 2014). Fly ash particles are characteristically spherical, and may be hollow or contain other smaller particles. It consists of a glassy phase and minority crystalline phase such as quartz, mullite and magnetite (Fernández-Jiménez and Palomo 2003). Fly ashes consist mainly of SiO_2 , significant quantities of Al_2O_3 , and limited amount of CaO , the composition may

nonetheless vary depending on the type of coal used and the incineration process in place at the power plant.

Generally speaking, the alkaline activation of a silicoaluminous material (fly ash) can be introduced as a mix of an activator (normally liquid with very high alkali concentration) and solid materials with selectable condition (high curing temperature). The resulting paste can set and harden like a Portland cement. The process can be explained conceptually in terms of a polymeric model similar to the schemes proposed for the reactions leading to the formation of certain zeolites: the Al and Si dissolved in the medium react to form complex poly-hydroxy-silicoaluminate complexes (Palomo, Alonso et al. 2004, Weng, Sagoe-Crentsil et al. 2005, Fernández-Jiménez, Palomo et al. 2006).

1.3.2.1 Reaction model

Glukhovsky proposed a general model to describe and explain the activation reaction in this type of materials, in which identified three different stages (Glukhovsky 1994).

- ***First stage : destruction-coagulation***

This first disaggregation process entails the breaking of the Me-O, Si-O-Si, Al-O-Al and Al-O-Si bonds in the starting material (Shi, Fernández-Jiménez et al. 2011). This disaggregation of the solid phase may be governed by the formation of complex unstable products whose origin lies in the change in the ionic strength of the medium prompted by the addition of electron donor atoms. The reaction normally stated by the breaking of Si-O-Si bonds. The OH⁻ ions coming from the activator make this breaking. These ions redistribute electronic density around the silicon atoms and weaken the Si-O-Si and making them more susceptible to rupture. The presence of the alkaline cation neutralizes the resulting negative charge. The formation of Si-O⁻Na⁺ bonds hinders the reversion to siloxane (Si-O-Si).

- ***Second stage : coagulation-condensation***

In this stage, the accumulation of ionic species has beneficial to the contact between the disaggregated products. Then polycondensation begins. Silica monomers inter-react to form dimers, and then continue to react with other monomers to build polymers. The polycondensation rate is determined by the state of the dissolved ions and the existence or otherwise of the conditions

necessary for gel precipitation. The clusters begin to grow in all directions along with generating colloids, which were formed as results of the polymerisation of the silicic acid. The aluminates also precipitate in polymerization, isomorphically replacing the silicon tetrahedral. While the alkaline metal catalyses the reaction in the first stage, in the second it acts a structural component.

- ***Third stage : condensation-crystallization***

In this stage, the presence of particles from the initial solid phase, together with the appearance of micro particles resulting from condensation, furthers reaction product precipitation. The qualitative and quantitative composition of the products are related to the mineralogical component of the prime materials, the nature of alkaline activator and the curing condition, especially curing temperature.

The research on the alkaline activation of fly ash has been studied depth in recent decades. A mechanism model was proposed by Palomo et al. (Palomo, Alonso et al. 2004) to describe the process based on zeolite synthesis. This model contained two staged.

- ***Nucleation stage***

With the dissolution of the aluminates present in the ash and the formation, via polymerization, of complex ionic species (stage highly dependent upon thermodynamic and kinetic parameters and which would cover the first two stages proposed by Glukhovsky).

- ***Growth stage***

When the nuclei reach a critical size and the crystal begins to grow. This stage is very slow due to experimental conditions. The final result of the alkaline activation of fly ash is an amorphous matrix with cementitious properties whose main component is none other than N-A-S-H gel (also called a “zeolite precursor”).

The Fig.1.3.5 showed a more detailed structural model to explain N-A-S-H gel formation. It includes a series of stages. The source of aluminosilicate dissolves into several species, primarily silica and alumina monomers, when it comes into contact with alkaline solution. Then these monomers interact to form dimers, and the dimers react with monomers to form trimers, tetramers and so on. The

solution will reach saturation, along with the precipitation of an Al-rich, metastable N-A-S-H gel (Gel 1) as an intermediate reaction product (Fernández-Jiménez, Palomo et al. 2006). From the first few minutes to the first few hours, the content of Al^{3+} ion in the alkaline medium is high, which can explain the gel formation. Reactive aluminium dissolves more quickly than silicon because Al-O bonds are weaker than Si-O bonds (Palomo, Krivenko et al. 2014). With the reaction progressing, more Si-O groups in the original source of aluminosilicate dissolve, the silicon concentration raises in the reaction medium and its proportion in the N-A-S-H gel (Gel 2).

Figure 1.3.5 Model proposed for N-A-S-H gel formation (Fernández-Jiménez and Palomo 2005, Duxson, Fernández-Jiménez et al. 2007).

1.3.2.2 Structure of gel formed: N-A-S-H

Aforementioned, the main reaction production in the alkaline activation in low-calcium and silica-rich and alumina-rich materials is an amorphous alkaline aluminosilicate hydrate known as N-A-S-H gel. The gel is a three-dimensional skeleton with random distribution of silicon and aluminium (Fernández-Jiménez and Palomo 2003, Fernández-Jiménez, de la Torre et al. 2006, Provis and Van Deventer 2009). The secondary reaction products in this type of systems are zeolites such as sodalite, zeolite P, Na-chabazite, zeolite Y and faujasite.

Fig.1.3.6 exhibited the SEM micrographs of original fly ash and the reaction product generated in the alkaline activation. Anhydrous ash characteristically consists of a series of spherical particles of different sizes (with diameters normally ranging from 10 to 200 μm (Fig.(a)). Some of these spheres are hollow, while others house smaller spheres inside. In the Fig.(b), a SEM micrograph of a matrix after alkaline activation, which activated by 8M NaOH (85 °C, 20 h) was exhibited. A massive and uniform N-A-S-H gel was observed.

The secondary reaction products (zeolites) are also visible. In Fig.1.3.6 (c and d) showed two types of zeolites.

Figure 1.3.6 SEM micrographs: (a) original fly ash; (b) N-A-S-H gel; (c) zeolite P; (d) Analcime (Palomo, Krivenko et al. 2014).

The nanostructure of N-A-S-H gels formed in the alkaline activation of fly ash has also been widely studied (Palomo, Alonso et al. 2004, Fernández-Jiménez and Palomo 2005, Provis and Van Deventer 2009, Li, Sun et al. 2010). Fig.1.3.7 shows the ^{29}Si and ^{27}Al MAS NMR spectrums. The ^{29}Si MAS NMR spectrum for the anhydrous ash is substantially different from the post-activation spectra. From 2 to 8 hours, early reaction stages, the most prominent changes occurred. The signal located at round -86 ppm was most intense, which was related to the formation of an aluminium-rich N-A-S-H gel with a predominance of Q^4 (4Al) environments. The signals detected at higher shift values (around -80 , -77 and -72 ppm), who's intensity declined with the progressing of the reaction, were associated to the presence of less condensed units (monomers and dimers). Assigning signals located at chemical shifts of under -88 ppm is complex because they overlap with the signals generated by the unreacted ash. As the reaction progressed (24 h and 7 d) the spectra changed substantially. Five signals were clearly visible at around -110 , -104 , -98 , -93 and -88 ppm, respectively attributed to the presence of silicon tetrahedra surround by zero $\text{Q}^4(0\text{Al})$, one

$Q^4(1Al)$, two $Q^4(2Al)$, three $Q^4(3Al)$ and four $Q^4(4Al)$ aluminium tetrahedra, indicative of a N-A-S-H gel with a higher silicon content (Gel 2).

Figure 1.3.7 (a) 8-M ^{29}Si MAS NMR spectra and (b) ^{27}Al MAS NMR spectra for anhydrous fly ash; and ash alkali-activated with 8M NaOH at 85 °C for 2 hours; 5 hours; 8 hours; 20 hours and 7 days (Fernández-Jiménez, Palomo et al. 2006).

Duxson et al. (Duxson, Lukey et al. 2005), analysing the ^{23}Na spectra generated in gels formed in the alkaline activation of metakaolin, concluded from the two signals observed at around -4 and 0 ppm that sodium can neutralize the excess negative charge in two ways. The -4 ppm signal was attributed to sodium associated with aluminium in the gel structure (offsetting the excess negative charge). The signal at 0 ppm, which only appeared in spectra for alkaline aluminosilicate gels with Si/Al ratios of under 1.4, was associated with the sodium present in the pore solution, which neutralises the negative charge in the $Al(OH)_4^-$ groups.

Criado (Criado, Fernández-Jiménez et al. 2008) also studied the position of sodium in the N-A-S-H gel formed during fly ash alkaline activation. In dehydrated zeolites the sodium ions were coordinated directly with oxygen anions, translating into signals located at very negative chemical shifts (around -20 ppm). Garcia-Lodeiro (García - Lodeiro, Fernández - Jiménez et al. 2010), analysed the ^{23}Na MAS NMR spectra generated by synthetic N-A-S-H gels, confirming the presence of a sole signal located at around -10 ppm, likewise related to partially hydrated sodium ($Na(H_2O)_x^+$).

1.3.3 Alkaline activation of hybrid alkaline cement: Group 3.

In recent studies, the potential for combining OPC and alkaline cement systems has been explored by some authors. These materials are known as hybrid alkaline cement (García-Lodeiro, Maltseva et al. 2012, Fernández-Jiménez, Flores et al. 2013, Palomo, Maltseva et al. 2013). The hybrid cementitious systems most frequently studied include the following blends:

- Portland cement + blast furnace slag
- Portland cement + phosphorous slag
- Portland cement + fly ash
- Portland cement + steel mill and blast furnace slag
- Portland cement + fly ash and blast furnace slag
- Multi-constituents

In these systems, the starting solid comprises small percentages (20 to 30 wt %) of OPC or PC clinker and large proportions (70 to 80 wt %) of raw aluminosilicate materials (See Figure 1.3.1). Generally they contain a separate source of alkali. The reaction products of hybrid alkaline cement system are intricate mixes of different gels, the type of products formed depends largely on different components of raw materials and the reaction conditions. Prior research has been illustrated the possibility that the cementitious gels, C-S-H and (C, N)-A-S-H, co-precipitated in hybrid alkaline cement hydration as main reaction products (Alonso and Palomo 2001, Puertas and Fernández-Jiménez 2003, Yip, Lukey et al. 2005, García-Lodeiro, Fernández-Jiménez et al. 2013, Garcia-Lodeiro, Fernandez-Jimenez et al. 2013). Meanwhile, the products (different gels) do not develop singly as separate gels but interact and undergoing structure and compositional change in the process (Garcia-Lodeiro, Palomo et al. 2011).

In 2005, Yip et al. studied the co-existence of the two gels, C-S-H and geopolymer, in the alkaline activation of blends of slag and metakaolin. Using scanning electron microscope (SEM) techniques, these authors proved that the co-precipitation of the two gels was possible, albeit highly conditioned by system alkalinity. The two gels only co-precipitated at low pH values. In the presence of high (7.5 M) NaOH concentrations, the geopolymer predominated and took up small amounts of calcium. The two phases were only observed to co-exist where a sufficient source of reactive calcium was present.

In the year 2007, Palomo et al. (Palomo, Fernández-Jiménez et al. 2007) studied a hybrid system containing minority (30 %) proportion of Portland cement clinker and high (70 %) fly ash contents. Deionized water and two alkaline solutions (NaOH, NaOH + waterglass) were used to hydrate with the materials.

Both the mechanical behaviour and the reaction products were analysed in 2 and 28 days. The results illustrated that Portland cement hydration is affected by alkaline content (OH^- concentration) and the presence of soluble silica. At the same time, the activation of fly ash at ambient temperature was accelerated by the presence of Portland cement clinker. It confirmed that the hydration of Portland cement clinker favoured the conditions for the consequent activation of fly ash by heat released during hydration, which induced ash dissolution, setting and hardening.

Figure 1.3.8 (a) 28-day BESEM micrograph of the cementitious matrix (70% FA+30% CK) in the system hydrated with solution (NaOH + Wg); **(b)** ^{29}Si MAS NMR spectra: A: initial anhydrous blend; B: 28-day water-hydrated blend; C: 28-day NaOH-hydrated blend; D: 28-day NaOH+Wg-hydrated blend (Palomo, Fernández-Jiménez et al. 2007)

The micro- and nano-structural characterization of the pastes generated in the aforementioned systems showed that a complex mix of amorphous gels (C-A-S-H, (N, C)-A-S-H) precipitates in activated systems (see Fig.1.3.8a). In the Fig.1.3.8b shows the ^{29}Si NMR spectra of the cementitious matrices. The signal at -86 ppm in spectra C and D is particular important. This signal could be related to either typical C-S-H gel (Q^2 (0Al) units) (Grutzeck, Benesi et al. 1989, Cong and Kirkpatrick 1996) or typical environments of N-A-S-H gel (Q^4 (3Al) and Q^4 (4Al) units) (Palomo, Alonso et al. 2004, Criado, Fernández-Jiménez et al. 2008). The signal at around -72 ppm has been associated with the presence of

anhydrous silicates which declined (was hydrated) in this system. The results confirmed the fact that both gels precipitated in this alkaline system (clinker + fly ash).

García-Lodeiro et al. (García-Lodeiro, Fernández-Jiménez et al. 2010, García Lodeiro, Fernández-Jiménez et al. 2010, Garcia-Lodeiro, Palomo et al. 2011) used synthetic gel phases to study the interaction of gels. The authors have provided much valuable information as following: The Ca / Si ratio in C-S-H gel declined in high alkaline media ; When C-S-H gel was exposed to both an alkali and soluble Al, it evolved into a more highly polymerized C-A-S-H gel; When mixed the synthetic C-S-H and N-A-S-H gels, the system tended toward the most stable C-A-S-H gel at pH > 12 environment.

Figure 1.3.9 Changes in gel composition and microstructure of a hybrid alkaline cement with a very high fly ash content: (a) initial stage; (b) early age sample (min); (c) early age sample (hours); (d) 7-days sample; (e) 28-day sample (adapted from (García-Lodeiro, Donatello et al. 2016)).

The same research group (García-Lodeiro, Donatello et al. 2016) proposed a sketch based on the BSEM (Backscattering electron microscopy) images of several hybrid alkaline cement samples to describe the co-precipitation process (see Fig. 1.3.9). At early age, because of the alkali (NaOH), substantial amounts of N-A-S-H gel and smaller quantities of C-S-H gel would be precipitated. Then liquid phase alkalinity starts to decline due to both carbonation and the alkaline hydrolysis of vitreous fly ash phase. C-S-H gel stability rises. As significant amounts of soluble Al are released by the fly ash, however, C-A-S-H gel

prevails over C-S-H gel formation. As a result of the presence of clinker, the pure N-A-S-H-like gel is unlikely in fly ash activation in hybrid alkaline cement than in clinker-free pure alkali-activated fly ash cements. It could be associated with more Ca released coming from clinker which lead to the partial replacement of Na^+ ions by Ca^{2+} ions as charge balance. Then an (N, C)-A-S-H gel (could be labeled) was formed.

1.3.3.1 Mechanism Model of C-S-H and N-A-S-H co-precipitation to make C-A-S-H gel

The research conducted on hybrid cements appears to clearly show that the type and characteristics of the gels formed are significantly impacted by the working conditions (pH and curing temperature) and the calcium concentration in the system.

^{29}Si and ^{27}Al NMR, together with TEM / EDX analysis of hybrid alkaline cements hydrated for up to one year have shown that both C-S-H and N-A-S-H gels evolve toward cross-linked C-A-S-H gels (García-Lodeiro, Fernández-Jiménez et al. 2013). The authors found that the lack of sufficient total Ca in the paste prevented conversion of all the N-A-S-H to C-A-S-H gel. In a recent study (García-Lodeiro, Donatello et al. 2016); the expected nano-structure gel evolution was presented. The activation model is illustrated in the Fig.1.3.10. It contains five steps:

- ***Dissolution of ionic species from the source of aluminosilicate (Fig.1.3.10a).*** The process begins with this dissolution in the alkaline solution, with the concomitant release of a wide variety of dissolved species. The medium becomes saturated with ions that are not uniformly distributed but rather exhibit local concentrations of the various species, depending on the nature of the nearest particle (García-Lodeiro, Fernández-Jiménez et al. 2013).
- ***Precipitation of aluminium-rich (type I) N-A-S-H gels and C-S-H gels (Fig.1.3.10b).*** In this step, when these local concentrations reach saturation C-S-H and N-A-S-H gels precipitate simultaneously (competitive reactions), although which of the two precipitates more rapidly has yet to be determined.

- ***Silica uptake by both gels with an increase in C-S-H gel means chain length and the generation of silica-high (type 2) N-A-S-H gels (Fig.1.3.10c).*** As the reaction progresses, more Si-O groups dissolve out of the initial aluminosilicate and the calcium silicate in the cement, raising the silicon concentration in the reaction medium and with it silicon uptake in both gels.
- ***Diffusion of aluminum and calcium in the matrix and their uptake, respectively, in C-S-H and N-A-S-H gels to form (N, C)-A-S-H gels (Fig.1.3.8d).*** The Ca^{2+} and Al^{3+} ions present in the aqueous solution begin to diffuse through the hardened cementitious matrix at almost the same time. A small number of Ca^{2+} ions that not taken up in the C-S-H gel interact with the N-A-S-H gel to form an (N, C)-A-S-H gel. Given the similar ionic radius and electronegative potential in Na^+ and Ca^{2+} , calcium replaces the sodium ions via ion exchange reminiscent of mechanisms observed in clay and zeolite (Lechert 1988, García-Lodeiro, Fernández-Jiménez et al. 2010). Maintaining the three-dimensional structure of the (N, C)-A-S-H gel (Garcia-Lodeiro, Palomo et al. 2011). The C-S-H gel which is formed from the silicates in cement takes aluminum into its composition in bridge positions (Richardson, Brough et al. 1994, Pardal, Pochard et al. 2009, Richardson 2014), yielding C-(A)-S-H $\rightarrow$ C-A-S-H gels as the aluminum content rises.
- ***Distortion of the (N, C)-A-S-H gel, leading to its rupture, while the C-A-S-H gel continues to take up aluminum species in bridging positions, favoring chain cross-linking and hence a more polymerized structure (Fig.1.3.8e).*** In this stage, calcium continues to diffuse through the pores of the matrix and interact with the (N, C)-A-S-H gel where a sufficient store of the element is available. The Si-O-Al bonds are distorted by the polarizing effect of the Ca^{2+} (to form Si-O-Ca). This process induces stress and ultimately ruptures. At present, two hypotheses can explain the ion exchange mechanisms between the different gels produced in these types of cementitious systems: (a) two ions of Ca^{2+} replace one Al^{3+} and one Na^+ ; (b) one Ca^{2+} replaces two ions of Na^+ . As the N-A-S-H gel releases aluminum, less polymerized structures (C-A-S-H gels) will be formed. At the same time, that C-A-S-H gel formed in previous stages will incorporate more silicon and aluminum ions in bridging positions (Sun, Young et al. 2006). The authors consider that alkalis released to the pore solution in the hydration process might react with unreacted

aluminosilicate particles, such as fly ash, then forming more (N, C)-A-S-H gels which could continue to interact with C-S-H.

Figure 1.3.10 Nano-structure mechanism for gel formation in hybrid alkaline cements.

1.3.3.2 The role of activator

The vast majority of hybrids cement hydration studies have been conducted with activators (primarily NaOH or mixes of NaOH + WG) that render the medium highly alkaline (Donatello, Fernández-Jimenez et al. 2013, Kang, Ge et al. 2015, Garcia-Lodeiro, Donatello et al. 2016). The high alkalinity of these solutions (with pH values of over 13) favors speedy ash dissolution. Moreover, at ambient

temperature fly ash activation is accelerated by the presence of Portland cement clinker. The explanation for this beneficial effect lies in the heat released during cement hydration, which would favor the chemical reactions inducing ash dissolution, setting and hardening.

However some of the arguments against the use of the alkali technology to make cements have centred on practical health and safety issues around the preparation and storage of highly alkaline solutions on construction factory sites. Given that alkali-activated cements are often touted as low-CO₂ alternatives to PC, the associated CO₂ footprint of the alkali activators has come under scrutiny (Duxson, Provis et al. 2007). The manufacture of NaOH and Na₂SiO₃ are fairly energy intensive processes. As a general rule of thumb, Duxson et al. (Justnes and Østnor 2014) contended that the CO₂ footprint of manufactured NaOH and Na₂SiO₃ stands at around 1 t CO₂/t. Furthermore, in hybrid alkaline systems, highly alkaline activators appear to adversely affect C-S-H gel stability, the kinetics of clinker calcium silicate hydration or both.

All this makes that the use of solid activators in these cements is a more real option from the point of view of its technological application. The result has been a growing interest in ‘just add water’ hybrid alkaline cement formulations, in which alkali solid salts milder are used. If it is possible, salts from natural raw.

Recently a group of mildly alkaline activators are usually used to activate hybrid alkaline cement system, such as Na₂SO₄, Na₂CO₃, and K₂CO₃, K₂SO₄. The reaction product of on-going Portland cement clinker hydration, Ca(OH)₂, can raise the pH in the medium by their synergetic reaction (Zhang, Sun et al. 2000, Bernal, Mejía de Gutiérrez et al. 2012, Fernández-Jiménez, Zibouche et al. 2013, Abdollahnejad, Hlavacek et al. 2014), further to Eq. 1.3.1 (Garcia-Lodeiro, Donatello et al. 2016):

Where A is an alkaline cation, normally Na⁺ or K⁺, and B is the anion in the respective inorganic salt. For instance, according whether the activator is a carbonate or a sulfate, its reaction with Ca(OH)₂ produces calcium carbonate or hydrated calcium sulfate, then the alkalinity (pH) of the bulky cement matrix increased and creates favorable conditions for the consequent geopolymerization process though high alkaline A(OH). Eq. 1.3.2 and Eq. 1.3.3 show the reactions. In addition, the heat released during initial OPC hydration favors and expedited the dissolution of aluminosilicate materials at high pH

(Zhang, Sun et al. 2000, Justnes and Østnor 2014). As those milder alkalis are used, “Just add water” hybrid alkaline cement formulations have attracted wide interest.

Due to the industrial interest that has this option in this Ph.D. work the activator used in cement HYC and HYP is a solid activator. In this point it is interest indicate that this type of cement, both of them, have been fabricated in two cement plants. These cements are the result of industrial trials of research work; the type of activator used is a cocktail of inorganic salts with the main component of Na_2SO_4 . Meanwhile, as the solid activators have been dosed in fabrication stage, this two hybrid alkaline cements could be hydrated with “just water” rather than alkaline solution, as a normal OPC hydration.

1.4 Temperature durably considerations

Durability is the ability to last a long time without significant deterioration. A durable material helps the environment by conserving resources and reducing wastes and the environmental impacts of repair and replacement. The production of replacement building materials depletes natural resources and can produce air and water pollution. The design service life of most buildings is often 30 years, although buildings often last 50 to 100 years or longer (Langston 2014). The problem of durability is extremely complex insofar as it depends on the material itself, on the design of the mixture, on the construction practice, on the environmental exposure conditions and on the provision of services.

Durability of OPC-based cement and concrete depends upon the following factors: cement content, compaction, curing, cover and permeability. In the literature there have a few papers explained those topics (Osborne 1999, Richardson 1999, Gonen and Yazicioglu 2007). However respect to the other cements considerer in this Ph.D. Work, alkali cement and hybrid cement, the knowledge is relatively low, especially in the second one. It is very difficult to study all this factors in depth in a single work, for them the effect of curing temperature when the cement is in fresh condition, in the early 20 hours have been selected (more information in section 1.4.1).

The main durability problems that can present the mortar and concrete are most directly related to their interaction with the environment during their time of service. There are many types but the major Concrete Durability types are:

- **Physical durability** against the following actions: Freezing and thawing action; Percolation / Permeability of water; Temperature stresses i.e. high heat of hydration
- **Chemical durability** against the following actions: Alkali Aggregate Reaction; Sulphate Attack; Chloride Ingress; Delay Ettringite Formation; Corrosion of reinforcement.

As with the factors mentioned above, there are many causes that justify the durability problems. Again the studies of these agents on mortars and concretes are very numerous not so much with regard to alkali cements and hybrid cements ([Donatello, Kuenzel et al. 2014](#)). In any case the factor selected was the behaviour at high temperatures. This effect is still poorly understood. In section 1.4.2 a background will be introduced.

As will be more detail indicated in the objective-section, in this thesis it was decided to study the effect of temperature on more sustainable cements (low clinker contents). In two cases, at initial ages (cured at 25 °C or 85 °C) and when cements are exposed to high temperatures (between 200 °C to 1000 °C).

1.4.1 Effect of curing-temperature

Proper curing of concrete is crucial to obtain design strength and maximum durability, especially for concrete exposed to extreme environmental conditions at an early age. It is known that Portland cement hydration is affected by many variables: chemical composition, water / cement ratio, presence of mineral additions, etc. Yet another variable, however, is regarded to play a key role, is curing-temperature. Temperature affect the development of mechanical strength, the microstructure of the paste, the nanostructure and composition of the gel, and the durability (especially to the know phenomenon called as delayed ettringite formation ([Taylor, Famy et al. 2001](#))). Temperature also plays an important role in the precast industry, because many of the concrete-precast products are manufactured at high curing temperatures.

Curing temperature below 10 °C, are not desirable for early age strength development. When the curing temperature is below (-10 °C) the cement hydration process may cease. Concrete needs to be kept for a longer time in

formwork when cast in cold weather condition. On the other hand, it is known that high curing temperature accelerates the hydration rate in all cement phases, raising early age strength, whereas older age performance is better in ambient than high temperature-cured cement (Escalante-García and Sharp 1998, Lothenbach and Wieland 2006). The reason for these observations is that a high initial rate of hydration induces the non-uniform distribution of the hydration product across the microstructure, with dense clusters forming around the hydrating grains and retarding subsequent hydration. The resulting increase in porosity has an adverse effect on long-term strength. A study on porosity of early age showed that at 85 °C total 28-day porosity increased by more than 20 % due to rising meso- and macro-porosity, which would explain the decline in strength in pastes cured at 85 °C. Such greater porosity also makes cement pastes more vulnerable to chemical attack by aggressive agents, reducing the service life of structures (Kjellsen, Detwiler et al. 1991, Kjellsen and Detwiler 1992, Al-Dulaijan, Al-Tayyib et al. 1995).

High temperatures likewise alter C-S-H gel composition. Curing temperature has a visible effect on C-S-H gel structure. The degree of C-S-H gel polymerization rises when temperature hydration increases. I. Elkhadiri and F. Puertas (Elkhadiri, Palacios et al. 2009) found that increasing the curing temperature from 20 to 85 °C raised the average C-S-H gel chain length dramatically, from two to eight links, even after only two days.

By the durability point of view the scientific literature indicates that high temperature curing in concrete is one of the factors that can lead to delayed ettringite formation (DEF) and concrete damage. As a consequence, standard of some country limit the maximum concrete curing temperature to 60 °C for concrete that will be exposed to “damp” conditions while in service. The current guidelines for the Precast/Pre-stressed Concrete Institute allow concrete to be cured to a concrete temperature of 82 °C, unless a known potential for alkali-silica reaction (ASR) or DEF exists, in which case the maximum recommended concrete curing temperature is 70 °C.

However in alkali activated fly ash-cement, curing temperature is very important, Palomo et al. (Palomo, Grutzeck et al. 1999) showed that a week at 65 °C or 24 h at 85 °C is enough to reach an acceptable reaction degree from the technological point of view. It is interesting to observe that, for a short time of reaction, the increase of the curing temperature from 45 °C to 65 °C increases by five times the velocity of mechanical strength development; and the increase of curing temperature from 65 °C to 85 °C increases by ten times this velocity. This

is due to the temperature improve the dissolution of the raw materials. As the temperature of reaction increases, the mechanical strength development increases also. However, there is a threshold value for mechanical strength development, above which the strength-gaining rate is slow.

In hybrid cement the effect of curing-temperature is not clear. At the moment researches in this field are practically non-existent. Would be interesting to know if these hybrid cement have behaviour more similar to Portland cement or to alkaline activated Fly ash-cement.

1.4.2 Behaviour at high temperature

Fire played and still played an important role for all cultures and religions. It has several symbolic meanings, from inspiration to hell, and has been regarded as the means then can warm and illuminate but at the same time can cause pain and death to human beings. Therefore, the feat of uncontrolled fires and the attempt to avoid their consequences were and still remain an important objective for human civilization, at the same time, the fire represents one of the most severe environmental condition to which structures may be subjected. Compared with wood and plastic, cement based materials offer safety advantage due to the nature of non-flammable as well help protect steel rebar in structural concretes. However, fire events and high temperature exposure can cause damage to cement-based materials, especially PC based materials.

The literature ([H.F.W.Taylor 1997](#)) universally acknowledges C-S-H to be primarily responsible for the mechanical properties of Portland cement and the concretes made from it. This gel is also generally recognized to decompose under high temperatures. At temperatures of around 300 to 400 °C, for instance, cement paste shrinks as water evaporates out of the C-S-H gel, possibly causing the material to burst. Exposure to high temperatures (over 450 °C) also causes portlandite to decompose into calcium oxide and water. At this temperature water is in gaseous form. The combined positive pressure of the water vapour and the entrained air ruptures the internal walls of the microspores causing an overall decline in cement paste strength due to the appearance of micro-cracks. Moreover, the calcium oxide formed is a very hygroscopic compound whose volume increases as it rehydrates.

The enormous pressure generated reduces compressive strength even further and may even cause structural collapse. Consequently, the threshold temperature at which the effects on the pore structure of concrete are irreversible may be

defined to be between 600 and 700 °C. When exposed to higher temperatures, the material collapses.

Davidovits summarized the physicochemical characteristics of alkali-activated binders to describe the potential as suitable candidates applied in high temperature environments (Davidovits 2008).

- They are totally inorganic polymeric materials therefore are incombustible
- They have ceramic-like properties that render them resistant upon heating at high temperature due to formation of several crystalline aluminosilicate phases with potentially high melting points. Therefore, they retain their structure integrity at elevated temperatures.
- They are endothermic materials due to the contained geopolymeric water (physically and chemically bound water) and therefore have high potential to absorb heat due to high heat capacity of water. The endothermicity of materials is a well-established and proven property in fire engineering application.
- They have thermal conductivity values in the region of 0.1-0.3 W/m.K, which is relatively low in comparison to the other commonly used structural building materials and almost identical or comparable to the marketable fire resistant materials (Sakkas, Nomikos et al. 2013). Therefore, alkali-activated binders have the ability to operate as an efficient heat flux barrier (Giannopoulou, Dimas et al. 2009).

The above summaries give alkali-activated binders opportunity for passive fire protection application under intermediate exposure temperature (< 900 °C). Materials with high fire resistance ratings can be produced that are capable of withstanding exposure temperatures as high as 1350 °C by controlling the chemical composition of alkali-activated binders (Sakkas, Nomikos et al. 2013).

There are very few studies on the behaviour of alkaline activated binders at elevated temperatures, especially binders of group 2 and group 3. Rovnaník (Rovnaník, Bayer et al. 2013) investigated the effect of high temperature on the solution (**Group 1**). Then the specimens were exposed to 200, 400, 600, 800, and 1200 °C for one hour. After high temperature treatment, the samples were cooled with two different ways (air and water). The compressive strength increased slightly at 200 °C and then decreased between 400 and 800 °C. Around 1000 °C, the compressive strength increased again. The authors explained that the increased mechanical property was related to the presence of compound crystallized akermanite, which was detected by ATD and XRD after 800 °C.

Barbosa and Mackenzie (Barbosa and MacKenzie 2003) studied the thermal behaviour of inorganic geopolymers and composites derived from metakaolinite with different $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratios (**Group 2**). Sodium polysialate polymers of suitable composition for optimum curing were remarkably thermally stable until the onset of melting at about 1300 °C. In addition, good thermal behaviour also observed in the composites consisting of a matrix of granular inorganic fillers up to 1000 °C.

Fernández-Jiménez and Jose Ygnacio started to investigate the high temperature performance of alkali-activated cementitious materials (Fernández-Jiménez, Palomo et al. 2008, Fernández-Jiménez, Pastor et al. 2010). Three binders were studied: (a) Portland cement (control); (b) sodium silicate activated fly ash (**Group 2**); (c) 70% ash + 30% clinker activated with solid-state activator (solid sodium silicate + Na_2CO_3 , **Group 3**). In-situ mechanical tested was conducted on the specimens to determine the change of mechanical properties and fracture toughness at elevated temperature (200, 400, 600, 800 and 1000 °C, Fig. 1.4.1). The alkali-activated fly ash cements performed better than traditional Portland cements when exposed to high temperature. Around 600-700 °C, a formation of molten phase were observed due to the high alkali content, with the solidification of that phase during cooling process, it is could be explained the better performance of high temperature resistance. In addition, the study also showed that the hybrid alkaline cements (**Group 3**) exhibited intermediate behaviour between the pure fly ash and pure Portland cement materials.

Figure 1.4.1 Mechanical strength, Trial 1: “high-temperature strength test”: (a) flexural strength; (b) compressive strength. (c) Fracture toughness versus temperature.

Shane Donatello et al. (Donatello, Kuenzel et al. 2014) investigated the physical and chemical changes taking place in a very high volume fly ash cement paste (FAN-4, 75 % fly ash + approximately 20% clinker + 5 % solid activator

(*Group 2*)), and OPC paste (as reference, called MS) when exposed to high temperature up to 1000 °C. FAN-4 pastes were mixed with distilled water and cured at room temperature then they were left to continue curing in the humidity chamber for 70 days before subjected to high temperature (200, 400, 600, 800 or 1000°C, 1 hour). Around 800 °C, the FAN-4 paste performed better mechanical performance. The Fig.1.4.2 exhibited the ternary diagram ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$) relating the major elemental compositions of MS and FAN-4 cements after 800 °C, which indicated the shifts to specific crystalline phase. It was clearly observed a well-balanced divergence of new crystalline phases in heated MS pastes and higher Ca content gehlenite was favored over lower Ca anorthite. As well, the diagram demonstrated that the Al-rich and low Ca content pastes prohibit the formation of larnite.

Figure 1.4.2 Illustration of the location of OPC and FAN-4 cement on ternary diagrams for $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$. Arrows indicates the shift to crystalline phases after firing at 800°C as implied by XRD data. Phase labels correspond as follows: Alb.=albite ($\text{NaAlSi}_3\text{O}_8$); Anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$); Geh.=gehlenite ($\text{Ca}_2\text{Al}(\text{AlSiO}_7)$); Lar.=larnite (Ca_2SiO_4); Mul.=mullite ($3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$); Nep. = nepheline ($\text{AlNa}(\text{SiO}_4)$); Wol. = wollastonite (CaSiO_3) (Donatello, Kuenzel et al. 2014).

In a recent paper (Martin, Pastor et al. 2015) studied the mechanical behaviour at temperature of alkali-activated aluminosilicates (geopolymers, over 600 °C) in situ and also the pseudo-plastic behaviour in vivo trials at high temperature (200-1000 °C). Three original materials were used in this study: (a) A type of OPC, as reference; (b) Fly ash (FAWN); (c) 85% fly ash+15% Bauxite

(FBxWN). In alkaline cements, irrespective of the type of trial (in vivo or post-firing), bending and compressive strength, fracture toughness and modulus of elasticity maintained or increased with temperature, at around 25–600 °C. As well, the decline in mechanical strength of alkaline cements during trials was observed due to the formation of a pseudo-viscous phase at around 600 °C. The Fig.1.4.3 plots porosity and pore size distribution in the cooled alkaline cements versus firing temperature. The most prominent changes were observed at 600, 800 and 1000 °C. The author explained the process as water transformation, from liquid water to water vapour, which the water tended to escape, generating pressure on the pore walls and intensifying inter-pore connections to the detriment of smaller pores. The pore structure plays an important role in the mechanical properties.

Figure 1.4.3 Variation in porosity and pore size distribution with temperature in alkaline cements: (b) FAWN and (c) FBxWN (Martin, Pastor et al. 2015).

Van Riessen et al (Provis and Van Deventer 2009) compared the behaviour of a fly ash-based geopolymer concrete and a Portland cement concrete, both with a compressive strength of approximately 75 Mpa at elevated temperature. The specimens chosen with 780×360×360 mm size and reinforced with 100×100 mm steel mesh with a bar diameter of 6 mm. All the specimens were exposed to the Eurocode EN1991-1-2 standard hydrocarbon fire on one side. Severe spalling was observed on the Portland cement concrete at the end of the fire test. On the contrast, no spalling phenomena appeared on the geopolymer concrete, which thus exhibited very good fire resistance performance.

No spalling appeared in geopolymer concretes were also observed by some researchers (Zhao and Sanjayan 2011). Zhao et al. use two simulated fire tests (Test 1: rapid surface temperature rise exposure test and test 2: standard curve fire test) to conduct on concrete cylinders which made from geopolymer and

OPC respectively. The experiments comparing two different concretes in same strength level from 40 to 100 MPa. In both types of test, no spalling was found in geopolymer concretes, whereas the companion Portland cement concrete exhibited spalling. In Fig.1.4.4, the concrete cylinders after fire tests were exhibited. In both tests, only OPC concrete showed spalling. The finding indicated that when compared at the same strength level, the geopolymer concrete possesses higher spalling resistance in a fire than Portland cement concrete due to its increased porosity.

Figure 1.4.4 Geopolymer and Portland cement concrete cylinders after two simulated fire tests (Adapted from (Zhao and Sanjayan 2011)).

2 *Objective*

World cement production represented approximately 4.074 billion tonnes in 2015, as the introduction before. About 4.2 GJ of energy is required to produce 1 tonne of OPC, which result in approximately 0.8-1.0 tonne of CO₂. The environment issue of CO₂ emission has been promoted the production of new cement materials as a main task of research in cement industry. In cement industry, the reduction of clinker factor still plays an important role on the aim of decreasing greenhouse gas emission. Scientific community and cement manufacturers have been working on it for many years; the aforementioned introduction has included some discussion on it. This Ph.D. thesis is a work along this research line.

The main objective of this work is to study the effect of temperature on some specific cementitious binder materials with low clinker content. It contains: the effect of temperature on the early hydration process (in pre-curing process); the effect of high temperature on the hardened pastes (between 200 and 1000 °C).

In this Ph. D. work, four different cements were studied

- **OPC:** A commercial Portland cement Type *CEM I 42.5* as reference
- **HYC:** pre-industrial hybrid alkaline cements contain 30 % of Portland cement clinker, 70 % mix of slag, fly ash and little solid activator (in design).
- **HYP:** Pre-industrial cement: 50 % belite cement clinker and 50 % mix of fly ash and little solid activator (in design). Really this cement is pseudo-hybrid cement because the belite-clinker content is higher than 30% according to hybrid alkaline cements position (see Fig. 1.3.1). However due to this blend include a little solid activator and the fly ash content is also high (higher than normal standard), in this Ph.D. work this cement has been considered also as hybrid cement
- **FAN:** Alkali-activated fly ash binder (free clinker).

To achieve the main objectives, this project was divided into the following two parts of work:

- ***Establish optimal activation conditions to produce cementitious materials with good mechanical strength.*** Different ages (3, 28 and 90 days) paste and mortar samples were prepared, tested and analysed. Two pre-curing temperature, 25 °C (ambient temperature) and 85 °C were selected to use to

study the early hydration process of all materials (OPC, HYC, HYP and FAN).

- ***Determine the behaviour at high temperature (durability) of the four types of cements studied in pastes.*** The temperatures selected were between 200 and 1000 °C (in situ and post thermal treatment). At the same time, mineralogical and microstructural variations were tracked by different techniques.

Through the work proposed above, the following special objected were established:

- Better to understand the physical-mechanical, mineralogical and microstructural properties of hybrid alkaline cements with different chemistry components when they were hydrated under different curing conditions.
- To explain the hydration process of hybrid alkaline cements with solid activator by analysing the hydration products according to the present knowledge.
- To investigate the high temperature effect on the mechanical behaviour of the materials (in situ and post).
- To find the relationship between the elemental composition of material and the high-temperature performance by tracking the mineralogical and microstructural variations taking place in the materials when exposed to high temperature.

3 *Techniques and Experiments*

3.1 Instrumental techniques

The different instrumental techniques and equipment used in this Ph.D. thesis are presented in this chapter. They are employed to characterization of the starting materials and the main reaction products obtained after different curing temperature and after being exposed to high temperature.

3.1.1 X-ray fluorescence: XRF

The elementary chemical composition of all the starting materials was determined by the instrumental technique X-ray fluorescence (XRF). XRF is based on the irradiation of sample by a primary X-ray beam. The individual atoms hereby excited emit secondary X-rays that can be detected and recorded in a spectrum. The spectral lines or peaks of such a spectrum are similar to a bar-code and are characteristic of the individual atoms, that is, of the respective elements in the sample. By reading a spectrum, the elemental composition of the sample becomes obvious ([Klockenkämper and von Bohlen 2014](#)).

The study of materials by XRF was conducted by PHILIPS PW-1004 X-RAY spectrometer (Institute of Building Sciences Eduardo Torroja, CSIC), with an X-ray tube generator of Sc-Mo. Before analyzing the starting materials by XRF, the weight loss was determined by subjecting samples to a temperature of 1000 °C of one hour.

3.1.2 Laser diffraction particle size analysis

Laser granulometry test is often used to study the materials particle size. The analysis of the original materials in this Ph.D. work was conducted by Sympatec diffractometer (Institute of Building Sciences Eduardo Torroja, CSIC,) with a measuring range from 0.90 to 175 microns. The powder sample is placed in water (for fly ash) and isopropyl alcohol (for cements) suspension to remove the Van der Waals and electrostatic force between particles by ultrasonic.

3.1.3 Mercury intrusion porosimetry test: MIP

Measuring the percentage of pore size distribution and pore volume in pastes obtained after thermal treatment process was determined by mercury intrusion porosimetry. This technique has been developed to determine the pore size distribution and volume of solids in the range of the microspores where the gas

adsorption technique cannot be applied. This technique is based on the concept that mercury has a high surface tension and therefore non-wetting properties towards many solids and also has contact angle greater than 90° with most materials. It is a non-wetting liquid which was required to raise the pressure to force it into the pores. In 1921, the theoretical foundations was set and the equation was proposed by E. Washburn, then the first time to use the technique to tested some porous materials by penetration of mercury into pores was in 1945 by H. Ritter and L. Drake (Ritter and Drake 1945). After L. Edel'man et al. (EDELMAN, Sominskii et al. 1961) introduced MIP to concrete science, this technique became the most widely used method for determine the porosity characteristic of cement paste (Aligizaki 2005).

MIP for all the pastes was tested in a Micromeritics Autopore IV 9500 (Institute of Building Sciences Eduardo Torroja, CSIC), which the pressure reaches up to 32000 psi and the determination of pore sizes.

3.1.4 Isothermal conduction calorimetry

Conduction calorimetry is shown to be a useful technique for examining the hydration behaviour of different types of cement and phenomena such as early stiffening and setting (Bensted 1987). All stages taken place in the process of cement hydration could be clearly followed by the technique.

The study of hydration of cement pastes at different temperature is monitored on a driving isotherm calorimeter TAM Air Thermometric (Institute of Building Sciences Eduardo Torroja, CSIC), consisting channels of simultaneous measures. Cement samples were weighted and uniformly distributed in vials. Five-gram sample solid were used, with a liquid/solid ratio 0.5. The calibration baseline was established by recording the flow feat for quartz mixed in water with the same liquid/solid ratio. The pastes were mixed with deionized water by hand for three minutes prior to insertion in the calorimeter.

3.1.5 Differential thermal and thermo-gravimetric analysis: DTA/TG

The differential thermal analysis and thermo-gravimetric analysis were used in order to meet the physical and chemical transformations in hydrated pastes of different cements with temperature.

The equipment used was a DTA-TGA-DSC Q600 TA Instruments with double branches, one for sample and the other for reference (Institute of Building Sciences Eduardo Torroja, CSIC). The program of temperature setting was used as follows: the temperature was increased from 25 to 80 °C at 10°/min, and maintained at this temperature for one hour to ensure the loss of free water. Subsequently a ramp was used until 1050 °C with 4 °C/min. Platinum capsules and nitrogen flow (100 ml/min) were used. Approximately 20 mg of sample and the equivalent reference amount of Al₂O₃ were weighed. The sensitivity of the balance is 0.1 mg.

3.1.6 X-ray Diffraction: XRD and Rietveld quantitative analysis: XRPD

XRD analysis is based on constructive interference of monochromatic X-rays and a crystalline sample: The X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a refracted ray) satisfies conditions. The interaction of the incident rays with the sample produces constructive interference (and a refracted ray) Satisfy conditions When Bragg's Law ($n\lambda = 2d \sin\theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then a detected, processed and counted. By changing the geometry of the incident rays, the orientation of the crystal and the detector centered, all possible directions of the lattice diffraction should be attained (Barbara L Dutrow)

XRD analysis was conducted in a D8 ADVANCE diffractometer (Institute of Building Sciences Eduardo Torroja, CSIC), which manufactured by BRUKER-AXS consisting of a high voltage generator 4 KW ray tube. The samples were grounded until a grain size below 45 microns to ensure that the formed tablet has a perfect surface. CuK $\alpha_{1,2}$ radiation was used. The settings were: variable 6mm divergence slit; 2 theta: 5-60°; step time: 0.5s; step size: 0.02°

XRPD is a powerful method for determining the quantities of crystalline and amorphous components in multiphase mixtures.

According to the former research work of A. Fernández-Jimenez (Fernández-Jimenez, de la Torre et al. 2006), the standard α -Al₂O₃ was synthesized as follows: 6 g of γ -Al₂O₃ (99.997% from Alfa) was ground in an agate ball mill at 200 rpm for 30 min. The resulting powder was placed in a Pt crucible and heated

at 1200 °C for 4 hours. The oxide was allowed to cool to 150 °C around over 5 hours and ground at room temperature in an agate mortar for 5 min. The sample was subjected to a second thermal treatment at 1300 °C for 6 hours and then cooled as above. This standard was then ground in an agate mortar for 5 min and sieved ($< 35 \mu\text{m}$) prior to weighing. Each of the mixtures used for analysis was carefully ground in an agate mortar for 10 minutes; adding acetone to facilitate particle dispersion, and then heated at 60 °C. Around 30% (wt) of corundum was added, with the exact gently loaded (vertically) on an aluminium X-ray sample holder.

Rietveld refinement was used on the powder patterns, applying GSAS software with a pseudo-Voigt function and including a correction for asymmetry due to axial divergence. The crystal structures used to interpret the powder patterns were taken from the Inorganic Crystal Structure Database (ICSD).

3.1.7 Nuclear magnetic resonance / Magic-angle spinning technique: NMR / MAS-NMR

The main hydration products of cementitious materials are kinds of amorphous gels with low crystallization as introduced in first chapter. Therefore, nuclear magnetic resonance (NMR) spectroscopic technique is very useful because it allows us to study the structure of amorphous materials or low structural order materials, which it is difficult to study by other techniques. NMR spectroscopy observes atomic nuclei behaviour through the property which be named nuclear spin. The nuclear spin behaviour can be modified by the electrons in the vicinity of the nucleus (Engelhardt and Michel 1987).

The technique of magic-angle spinning (MAS) has been used to analyse aluminate, silicate, and alumino-silicate materials since about 1980, and spectrometers capable of performing such experiments have been widely available since about 1985 (Colombet, Grimmer et al. 2012).

^{29}Si and ^{27}Al NMR spectrum are the most common used two spectrums for studying the cementitious materials. For the presentation of the structure of building units or silicate anions in the following commonly used Q^n notation is adopted (Engelhardt and Michel 1987). Q represents a silicon atom bonded to four oxygen atoms forming a tetrahedron. The superscript n indicates the connectivity. Thus, Q^0 denotes the monomeric orthosilicate anion SiO_4^{4-} , Q^1 end-groups of chains, Q^2 middle groups in chains or cycles, Q^3 chain branching sites and Q^4 three-dimensionally cross-linked groups (see Fig.3.1.1 top). q^n notation

was used to present the structure of building units or aluminate anions. In the Fig.3.1.2, it shows the ranges isotropic ^{27}Al chemical shifts.

Figure 3.1.1 Top, notation for building units and silicate anions. Q^n units of silicates Bottom, ^{29}Si chemical shift ranges of Q^n building units in silicate solution.

Figure 3.1.2 Ranges of isotropic ^{27}Al chemical shifts in aluminate $[q^n(m\text{Al})]$ aluminosilicates $[q^3(3\text{Si}), q^4(4\text{Al})]$ and AlO_n polyhedral. $q^n(m\text{T})$ denotes tetrahedrally coordinanted aluminium-centred $\text{Al}(\text{OT})_m(\text{O})_{4-m}$ building unites (redraw from (Engelhardt and Michel 1987)).

The ^{29}Si and ^{27}Al MAS-NMR was conducted in a Bruker AVANCE-400 spectrometer (Institute of Materials Science, CSIC) under the following conditions:

^{29}Si resonance frequency, 79.5 MHz; spinning rate 10kHz; pulse sequence, single pulse (5 μs); recycle delay, 10 s; number of transients, 4912; external standard, TMS (tetramethylsilane);

^{27}Al resonance frequency, 104.3 MHz; spinning rate 10kHz; recycle delay, 5s; pulse sequence, single pulse (2 μs); number of transients, 400; external standard, $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

3.1.8 Scanning electron microscopy and energy dispersive X-Ray analysis: SEM/EDX

In this thesis the scanning electron microscopy (SEM) was used to obtain 1) the microstructure information of different cementitious material hydration products by collocating with the energy dispersive X-ray (EDX) analysis; and 2) the valuable information of fracture surfaces of pastes after exposing to high temperature. This study was carried out with:

(1) A JEOL 5400 spectrometer coupled to an energy dispersive X-ray of the brand OXFORD LINK-ISIS-EDX (Institute of Building Sciences Eduardo Torroja, CSIC). The samples were dried under vacuum and metalized with carbon for analysis by microscopy.

(2) A JEOL JSM 6300 scanning electron microscope with an energy dispersive X-ray (Department of materials science, ETSI, UPM). The fracture surfaces prepared for SEM were previously metalized by means of vacuum deposition of a gold layer using a Hitachi E-1030 sputter coater.

3.2 Experiments Methods

For achieving the aims of this work, some experiments were conducted to analyze materials and samples; as well several trials were designed to study the characteristics of them. Temperature, as the main line of this work, divided it into two parts: **1) Pre-curing temperature (20 and 85 °C); 2) High temperature (200-1000 °C)**. In this section, the experimental procedures used for sample preparation and methods applied for characterization study are exposed in details.

According to the experiments requests, mortars and pastes were prepared as per standard EN-196 with designed condition (liquid/solid ratio, sand/binder ratio, pre-curing temperature and curing conditions). The general experimental process was illustrated in Fig.3.2.1, to explain how the work undergone with time. The experiments progress is four steps as following.

Specimen's preparation: Mortars and pastes were prepared with different pre-curing conditions until the testing age.

Analysis and selection: The samples (mortars and pastes) were studied by different techniques to analyse the mechanical, mineralogical and microstructural properties under the effect of pre-curing conditions, in order to select suitable condition to prepare specimens for the next behaviour study of high temperature resistance.

Pastes preparation: With the results of the last step, new pastes sample (with selected preparation condition) were made and processed in laboratory and factory for being studied at in-situ/ post high temperature

Behaviour study: In this step, experiments were conducted on all material to study their behaviour when they were exposed to high temperature.

Figure 3.2.1 The flow chart of general experiment design

3.2.1 Specimen elaboration

Large amounts of mortars and pastes were elaborated in the laboratory for the study. Four size of samples were produced in the work, one size of prismatic ($40 \times 40 \times 160$ mm) mortar (See Fig.3.2.2, **No.1**) and three sizes of prismatic pastes ($10 \times 10 \times 60$ mm; $4 \times 4 \times 10$ mm; $4 \times 14 \times 50$ mm) were produced ((See Fig.3.2.2, **No.2**; **No.3**; **No.4** respectively).

According to the standard EN 196-1, the sample preparation information was listed in the Table 3.2.1. Deionized water has been used in the hydration of OPC, and two pre-industrial cements, HYC and HYP. Sodium hydroxide solution, a typical alkali activator, has been used to activate fly ash Lada. 8 molar Sodium hydroxide, NaOH*, solution was prepared with a commercial solid NaOH (from **Panreac**) with deionized water.

Table 3.2.1 Specimens elaboration information

Materials	Liquid /Activador	Mortar		Paste
		Liquid/Solid	Sand/Cement	Liquid/Solid
OPC	water	0.5	3/1	0.3
HYC	water	0.5	3/1	0.3
HYP	water	0.5	3/1	0.3
FAN	8M NaOH*	0.45	3/1	0.3

1. Mortar	$40 \times 40 \times 160$ mm
2. Paste	$10 \times 10 \times 60$ mm
3. Paste	$4 \times 4 \times 10$ mm
4. Paste	$4 \times 14 \times 50$ mm

Figure 3.2.2 Three-dimensional perspective model of sample in proportion.

3.2.1.1 Effect of pre-curing temperature: 25 and 85 °C

In this part of work, two pre-curing temperatures in the initial 20 hours were selected for study, Room temperature $25\pm1^{\circ}\text{C}$, and 85°C . The reason is, for normal Portland cement, at room temperature, the hydration process undergoes well and the early strength is high enough, however, for alkali-activated fly ash binder materials, higher pre-curing temperature is needed for activating the reaction between activator and fly ash in order to obtain mechanical strength. The former research (Palomo, Grutzeck et al. 1999, Criado, Palomo et al. 2005) indicated that 85°C was a selected pre-curing temperature for this kind of materials. According to the components of two type of pre-industrial cements, which contained fly ash and solid activator, this two pre-curing temperature were used as the study factor. The pre-curing process is described as followings.

At 25°C : Prismatic mortars and pastes (See Fig.3.2.2 , **No.1** and **No.2**) specimens were made in moulds and stored with moulds in climatic chamber ($25\pm1^{\circ}\text{C}$, 99% RH) for initial twenty hours. Then the specimens were removed from the moulds, and stored continually in climatic chamber until the testing age: 3, 28 and 90 days.

At 85°C : Prismatic mortars and pastes specimens (See Fig.3.2.2, **No.1** and **No.2**) were made in moulds. Then the specimens were placed in an individual plastic bag with a little water under the moulds. This bag was totally sealed by a cover to prevent water evaporation. Then they were introduced into an oven for the initial twenty hours at 85°C . After twenty hours, the bag with specimens was get out of the oven until room temperature. Finally, the specimens were removed from the moulds and stored in climatic chamber ($25\pm1^{\circ}\text{C}$, 99% RH) until the testing age: 3, 28 and 90 days.

After reach the testing age, 3, 28 and 90 days, the flexural strength of pastes ($1\times1\times6$ cm) were tested via three point bending (TPB) test with prisms centred upon two points spaced 50 mm apart in a machine Netch-401-2 (Fig.3.2.3a). A load is applied vertically with a rate of $50\text{ N/s} \pm 10\text{ N/s}$ until its failure. After the flexural strength test, a single fissure was produced in the centre of the prism. Then the two fragments were each then tested for compressive strength through the machine Ibertest Autotest 200-10 (Fig.3.2.3b) according to the standard UNE-EN 196-1.

The mortars was conducted in the model of machine Ibertest Autotest 200-10 (Fig.3.2.3b) at the same testing age (3, 28 and 90 days) as pastes, for the determination of flexural and compressive strength.

Figure 3.2.3 a) Machine Netch-401-2; b) Machine Ibertest Autotest 200-10.

When the mechanical test was finished, the pieces of pastes were collected and put inside acetone for several days. The hydration reaction of cementitious material was detained exactly at the testing age (3, 28 and 90 days) by acetone. Then the samples were removed from acetone and dried.

Parts of dried sample were milled to a fine powder (smaller than $45\mu\text{m}$) for analysis of XRD and MAS NMR (after removing of iron ions). Selected parts were analysed with SEM/EDX techniques, which polished sections were carbon-coated and studied under a JEOL JSM scanning electron microscope fitted with a solid-state BSE detector and a LINK-ISIS energy dispersive X-ray (EDX) analyser.

3.2.1.2 In-situ high temperature behaviour study: 200-1000 °C

In the study of in-situ high temperature behaviour, only pastes were used as specimens. To ensure sample uniformity, a single block ($100\times 100\times 60\text{ mm}$) of pastes was moulded for each cement. The conditions were listed in table 3.2.2. The pastes were stored in climatic chamber ($25\pm 1^\circ\text{C}$, 99% RH) for 28 days and after the pastes removing out of chamber, they were cut into two sizes of

specimens in the factory, $4 \times 4 \times 10$ mm; $4 \times 14 \times 50$ mm (See Fig. 3.2.2, **No.3**, **No.4**) for the testing of compressive and flexural strength respectively. The notch was introduced to the specimens of $4 \times 14 \times 50$ mm for fracture toughness test at high temperature.

Table 3.2.2 Specimens elaboration information

Materials	Liquid /Activador	Paste		
		Liquid/Solid	Pre-curing temperature (°C)	Test age (days)
OPC	water	0.3	25	28
HYC	water	0.3	25	28
HYP	water	0.3	25	28
FAN	8M NaOH	0.3	85	28

3.2.1.3 Post-thermal behaviour study

The intention of this test is to evaluate the residual strength after abrupt but not prolonged exposure to high temperature, in an attempt to simulate the conditions prevailing in the event of fire.

Prismatic pastes ($10 \times 10 \times 60$ mm) were prepared with the condition listed in Table 3.2.2. The paste samples were removed from the champers after 28 days and then weighed, measured prior to being exposed to high temperature for a period of 2 hours, at 400, 600, 800, and 1000 °C. Exposure was achieved by direct placement in an oven pre-heated to the target temperature. After removing from the oven, half of each sample batch was immediately left to cool on a ceramic plate in air and the other half was cooled by immersion in tap water for around 15 min, which is faster than in air. This process is an important consideration according to the fact that in real life, most fires issues are extinguished with water and the subsequent rehydration of fire damaged cement based materials is a particular concern ([Donatello, Kuenzel et al. 2014](#)).

After one night left on a laboratory bench for dry, the samples were reweighed and measured. Then the $10 \times 10 \times 60$ mm paste sample were tested for flexural strength. The flexural strength test produces a single fissure in the centre of the prism. The two parts were each then tested for compressive strength.

Strength of pastes not exposed to high temperature was also tested as a baseline control at 28 days.

After mechanical test, some fragment of each sample were ground to a fine powder ($<45\text{ }\mu\text{m}$) and analysed by XRD, DTA/TG, MAS NMR. Some selected fragments of sample were studied by MIP.

3.2.2 Advanced experimental methods: in situ mechanical tests.

These tests, which were designed to evaluate variations in mechanical performance with temperature, include compressive strength, bending strength and fracture toughness. These tests were conducted on an Instron model 3369 servo-mechanical testing machine (test-control part), inside which an MTS (USA) furnace (temperature control part) was installed to conduct the tests at high temperatures. See Fig.3.2.4.

- Test control part: crosshead displacements during the tests were measured with a linear variable differential transformer (LVDT) strain gauge (resolution $\pm 1\text{ }\mu\text{m}$) placed outside the furnace. The tests were run under displacement control at a loading speed of $200\text{ }\mu\text{m}/\text{min}$ for compressive test and $100\text{ }\mu\text{m}/\text{min}$ for bending test; the load was applied with high purity alumina (99.7 %) bars and cylinders.

- Temperature control part: the specimens were heated at dynamic rehearse with a rate of $5\text{ }^{\circ}\text{C}/\text{minute}$, similar to the temperature versus time curve defined by the standard ISO 834, up to $200\text{ }^{\circ}\text{C}$ to prevent the appearance of thermal gradients that might cause premature failure. Once the target temperature was attained, each specimen was stabilized for 15 minutes before the test was conducted.

The test machine output the value of displacement and load, after calculating, we can get stress-strain curves in the test. Two model of maximum stress are used to describing the mechanical property of cementitious binder material when exposed to high temperature. One is ultimate strength and the other is the yield strength at 0.2 % offset).

Figure 3.2.4 The in-situ high temperature testing system (Department of materials science, ETSI, UPM)

Figure 3.2.5 Theoretical stress-strain curve for a material, based on compressive or bending strength test (Martin, Pastor et al. 2015)

Fig.3.2.5 gives an example of a stress-strain curve for a theoretical material exhibiting plastic behaviour. According to this curve, in non-brittle failure material, the elastic zone is delimited by the yield stress (Point 2). The critical stress beyond which the material does not fully regain its original shape after the load is removed. It means that the materials are permanently deformed. When

the stress exceeds yield point, the material undergoes plastic deformation, exhibiting ductile behaviour.

3.2.2.1 Compressive test

The compressive mechanical tests were conducted on $4 \times 4 \times 14$ mm specimens (see Fig.3.2.6). The test was conducted on the Instron model 3369 servomechanical testing machine with a cross-head at a speed of $200 \mu\text{m} / \text{min.}$), inside which a MTS (USA) furnace. The specimens were subjected to a 5 ± 1 N preload during heating to fasten them securely to the testing device.

Figure 3.2.6 Schematic arrangement of compressive mechanical tests.

Stress-strain (σ - ϵ) curve was calculated from the load-displacement (F - δ) curve which was recorded by the program during compressive test according to the following equations:

$$\sigma_c = \frac{F}{A} \quad (3.2.1)$$

$$\epsilon_c = \frac{L - L_0}{L_0} \quad (3.2.2)$$

Where, L_0 (mm) is the height of the sample (original specimen length); F (N) is the applied load; A (mm²) is the cross-sectional area of paste specimen; L (mm) is current specimen length;

3.2.2.2 Flexural strength

The flexural strength was determined by non-standard three-point bending test (TPB) on the rectangular paste samples (4×14×50 mm), see Fig.3.2.7. The three-point bending test was conducted on the Instron model 3369 servo-mechanical testing machine with a cross-head at a speed of 100 μm / min. The loading direction is parallel to the planes of stacking tapes in the samples. These three-points bending tests were conducted with supports space at 20 mm intervals, in application of the Bernoulli theorem (Timoshenko and Young 1956). The specimens were subjected to a 2~3 N preload during heating to fasten them securely to the testing device.

Figure 3.2.7 the schematic arrangement of the three-point bending tests.

Engineering stress-strain (σ - ϵ) curve was calculated from the load-displacement (F - δ) curve which was recorded by the program during three-point bending test according to the following equations:

$$\sigma_F = \frac{3F}{2BD^2} \quad (3.2.3)$$

$$\varepsilon_F = \frac{6\delta D}{l^2} \quad (3.2.4)$$

Where l (mm) is the length of the support span, 20 mm; F (N) is the applied load; B (mm) is width of paste specimen; D (mm) is thickness of paste specimen; δ (mm) is the value of displacement of the central parts of specimen equal to the loading arm.

The static Young's modulus, E , was determined and calculated from the slope of the initial linear parts of the stress-strain curves with the following equation:

$$E = \frac{\sigma_F}{\varepsilon_F} = \frac{L^3}{4BD^3} \cdot \frac{\Delta F}{\Delta \delta} \quad (3.2.5)$$

3.2.2.3 Fracture toughness

Fracture toughness (K_{IC}) values are used extensively to characterize the fracture resistance of ceramics and brittle materials. Even fracture toughness for cement-based materials is not used as a design tool, the fracture behaviour is also very important for the structure of cementitious material. Many methods are developed to evaluate the fracture toughness of ceramic materials and method selection and resource materials can be dependent. During fracture toughness testing, to known flaw (e.g. notches or pre-cracks) is introduced into the materials for the determination of fracture energy, Which is required to be reliable, reproducible and avoid introducing unwanted damage, in order to create accurate test results. Due to the intrinsic brittle characteristics, ceramics are highly sensitive to generally flaws and the measurements of fracture toughness of ceramics are complicated. Therefore, it's crucial and to select a proper method to enter the pre-cracks or notches.

For this study, considering the effect of tip radius of notch on K_{IC} determination, Single edge V-notched beam (SEVNB) specimens were experimentally produced. In this method, a sharp razor blade of 150 μm thick that was regularly impregnated with diamond paste of 1 μm grain size wears the materials down because of the friction (Kübler 1999). This method has been applied to ceramics successfully due to the fact that these types of materials are more abrasive than the metallic blade. Meanwhile, the diamond paste sharpens the blade during notching and helps to generate a notch tip around a few microns.

To achieve the V-notches, a razor blade machine that works like a tribometer was specially designed (see Fig.3.2.8). In this machine, the specimen is placed in a clamp on a ground plate and the razor blade lies within a guide-way above. The upper part can move vertically to apply a normal force against the mounted specimen. The specimen moves linearly in the horizontal direction with an adequate frequency to create the V-notch. The frequency is controlled by the operator.

According to the former work (Teresa Palacios 2015), to obtain good results, several factors should be considered:

- The microstructure of materials and physical properties.
- The frequency of linear movement
- The normal force and its frequency
- The sharpness of the razor blade and the change of the razor blade
- The replenished of diamond paste
- The proper cleaning between razor blade changes

Figure 3.2.8 Razor blade machine to introduce the SEVNB specimens.

All the factors have an influence on introduce of V-notch. In the preparation of specimens, the operation should be controlled carefully by the person. There is no fixed setting. The process is time-consuming because these parameters need to be optimized for each materials and the subsequent notching process may last several hours for one specimen.

In the Fig.3.2.9, we can obtain that the introduced notch are very sharp, approximately 5-10 μm . For cementitious materials, the fracture toughness values obtained using SEBNB specimens could determine the real fracture toughness (Palacios and Pastor 2015).

Figure 3.2.9 Micrographs of a SEVNB specimen.

Figure 3.2.10 Schematic diagram of fracture toughness tests.

After introducing V-notches, the specimens were conducted on TPB test. The schematic diagram of fracture toughness tests was given in the Fig.3.2.10. Design failure was calculated from the equation for notched beams (Guinea,

Pastor et al. 1998), which according to three-point bending single-edge notched fracture test by introducing a sharp V type notch to the specimens.

After the notching process, the specimens with geometry of 4×14×50 mm were tested on a universal testing machine at different temperature, with a span length of 10 mm and a constant displacement rate of 0.1 mm / min. The load and load point displacement were continuously monitored using a load cell and a linear variable differential transformer induction transducer, respectively. Note that the loading direction was parallel to the planes of the stacking tapes in the tape casting samples. Each material was tested in three samples at target temperature. The following equation was used to calculate the failure fracture toughness:

$$K_{IC} = \frac{3lF_f}{2BD^{3/2}} \cdot \alpha^{1/2} \cdot \gamma \quad (3.2.6)$$

$$\gamma = \frac{A - C \cdot \alpha + E \cdot \alpha^2 - F \cdot \alpha^3 + G \cdot \alpha^4}{(1 + 2\alpha)(1 - \alpha)^{1.5}} \quad (3.2.7)$$

where:

$$\begin{aligned} A &= 1.989 - 0.356 \beta & C &= 1.217 + 0.315 \beta \\ E &= 3.212 + 0.705 \beta & F &= 3.222 - 0.020 \beta \\ G &= 1.226 - 0.015 \beta & \alpha &= a / D, \beta = D / l \end{aligned}$$

F_f is the applied load at failure, l is the length of the support span, B is width of specimen bar, D is thickness of specimen bar, a is V-notch depth, γ is the stress intensity shape factors.

After test, the fracture surface was metalized and analyzed with a scanning electron microscope SEM, in order to study the microstructure property of fracture surface at different temperature of selected cementitious materials.

4 Materials Characteristic

4.1 Introduction

In this part, different methodologies and relevant results will be described for the characterization of starting materials, including chemical and physical properties which intrinsically link with the cementitious binders. In this Ph.D. research work, three industrial / pre-industrial cements and on type of fly ash were studied. The information and abbreviation are given as following:

- **OPC:** One CEM I 42.5 commercial Portland cement, used as reference, manufactured in Spain.
- **HYC:** One pre-industrial hybrid cement, manufactured in a cement plant in Latin America, about 20 tons. The process, consisting in the joint milling of Portland clinker, slag, fly ash and solid activator, is depicted in Fig.4.1.1 The proportions used were 30 % Portland cement clinker + 32.5 % BFS + 32.5 % FA + 5 % solid activator¹.
- **HYP:** One pre-industrial hybrid cement, which manufactured in a cement plant in Western Europe, consisting 48 % Belite cement clinker + 47 % FA + 5 % solid activator*. The production process is similar to HYC.
- **FA:** One type F fly ash was studied as starting material of alkali-cement, which is from a coal-fired steam power of Lada in Spain.

Figure 4.1.1 Stage in HYC manufacture.

¹ **Solid activator***: the 5 % addition of solid activator to the raw hybrid cementitious materials was a cocktail of salts. The main salt is Na_2SO_4 of both hybrid cements (HYC and HYP, the composition is different). As introduced in section 1.3.3.2, Na_2SO_4 has been used as main mildly alkaline activator to activate hybrid alkaline cement system, although the real composition of the solid activator is confidential.

All the materials were analysed by XRF, XRD, XRPD, ^{29}Si and ^{27}Al MAS NMR in order to know clearly the chemical mineralogical and microstructural characteristics. The raw materials were also studied by Laser granulometry to test the particle distribution. The results will be introduced and discussed in this chapter.

4.2 Chemical composition

Chemical analysis of all materials was given by Table 4.1.1. The elemental chemical composition of each starting materials was obtained by X-ray fluorescence. In all cases, the loss on ignition is determined by calcinations of the sample at 1000 °C (UNE-EN-196-2:2005).

It (see Table 4.2.1) shows that CaO composition declines, on the contrary Al_2O_3 content increases among four materials (OPC-HYC-HYP-FA). The materials were selected to be studied in order to get binders materials with different chemical composition. The major elemental compositions of the raw materials were presented in the ternary diagram (SiO_2 - Al_2O_3 -CaO) in Fig.4.2.1. This ternary diagram illustrates a well linear relation of four materials. We have reason to believe that the chemical composition has an important influence on the cementitious materials' behaviour when they are exposed at high temperature.

Table 4.2.1 Chemical composition of the raw materials (% by Mass).

	OPC	HYC	HYP	FA
CaO	62.5	39.7	29.1	4.39
SiO₂	19.5	32.5	38.5	51.51
Al₂O₃	5.60	12.2	14.9	27.47
Fe₂O₃	2.31	3.83	4.93	7.23
MgO	0.77	0.94	2.18	1.86
SO₃	3.33	3.12	3.26	0.15
Na₂O	0.05	1.04	1.61	0.70
K₂O	1.03	0.78	1.61	3.46
TiO₂	0.24	0.50	0.86	/
MnO/Mn₂O₃	0.05	0.94	0.04	/
Other	1.41	1.90	0.27	1.37
LOI(Loss on ignition)	3.09	2.32	2.82	1.86

In the alkaline activation process of the fly ashes it is very important to know the percentage of “reactive silica” because reactive silica is the part of fly ash reacting with the alumina and the alkalis for giving place the cementitious material. Fly ash Lada presented the 42.17% reactive silica according to the

former work (Fernández-Jiménez and Palomo 2003), which determined according to the standard UNE 80225.

Figure 4.2.1 The $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ ternary diagram of raw materials (by mass).

4.3 Practical size distribution

Particle size distribution is the physical characteristic of cementitious materials strongly affecting their property as binder materials, partially on the strength. These parameters define the proportion of fine and coarse particles in the cement. This proportion control water demand, setting and hydration reactions (Kuhlmann, Ellerbrock et al. 1985, Sprung, Kuhlmann et al. 1985). For Portland cement, a wide range of particle size is necessary. As it reacts with water, a layer of hydration product started to form around the outside of the particles, which will separate the unreacted core of the particles from the surrounding water. This layer could slow down the hydration rate. However, too much small particles will lead to unexpected quick setting. At the same time, heat release, capillary porosity percolation, diffusivity, shrinkage and microstructure are also influenced by particle distribution (Bentz, Garboczi et al. 1999). The former study has reported that particle size in the range of 3-30 μm has strong influence on the strength, and particle size larger than 60 μm make practically no contribution to strength development (Škvára, Kolář et al. 1981, Qingyun 2005).

In the activation of aluminosilicates materials, the fineness strongly affected their reactivity (slag and fly ash). It is reported that around 80% amount of particles with a similar or lower size than $45\mu\text{m}$ was recommended of fly ash (Fernández-Jiménez and Palomo 2003). When the particle fraction size higher than $45\mu\text{m}$ was removed in the fly ash studied, the mechanical strengths increased remarkably.

Figure 4.3.1 Practical size distribution in materials for OPC, HYC, HYP and FA.

Table 4.3.1 Particle size under $45\mu\text{m}$ of all starting materials.

Particle size	Materials			
	OPC	HYC	HYP	FA
<45 μm (%)	89.16	94.97	96.58	78.50
<30 μm (%)	75.06	83.31	87.03	62.02

Particle size distribution was determined by laser granulometry with a measuring range of 0.90 - 175 microns. Further to the particle size distribution findings shown in Fig.4.3.1. The data particle size under $45\mu\text{m}$ and $32\mu\text{m}$ of all materials was given in Table 4.3.1. These results show that HYC and HYP have

a relatively similar size distribution, with a larger fine particle size than OPC. However, fly ash has larger particle size among the starting materials.

4.4 Mineralogical characterization

4.4.1 XRD analysis

The diffractograms for the starting materials were reproduced in the Fig.4.4.1. An analysis in the diffractograms of materials revealed the following.

OPC: The crystalline phases of typical clinker, alite (C_3S , $2\theta = 32.07^\circ$, 34.29° and 41.14°), belite (C_2S , $2\theta = 32.07^\circ$, 32.62° and 32.99°), calcium aluminate (C_3A , $2\theta = 33.15^\circ$, 47.63° and 59.25°) and ferrite phase (C_4AF , $2\theta = 12.20^\circ$, 33.88° and 50.25°) were detected. Gypsum ($CaSO_4 \cdot 2H_2O$, $2\theta = 11.59^\circ$, 20.72° and 29.11°) was also exhibited in XRD pattern (Fig.4.4.1A).

HYC: In addition to the crystalline phases typical of clinker (such as alite and belite, Fig.4.4.1B), the pattern for the starting cement HYC exhibited the mullite and quartz present in the fly ash and a hump across 2θ $25-35^\circ$, associated with the vitreous component in the slag and ash. Gypsum was also detected.

HYP: From the Fig.4.4.1C, we can see that the XRD pattern for HYP is quite different with OPC. A hump across 2θ $20-35^\circ$, associated with the vitreous component on the ash appeared. A high intense of peak which related to quartz was detected, for the reason of high component of ash. Mullite present in the ash was detected. The crystalline phases of clinker are also exhibited in the pattern.

FA: When we focus on the diffractogram of fly ash (Fig.4.4.1D), it shows that this is essentially a vitreous material (exhibited a characteristic hump of a major amorphous phase between 2θ $20-35^\circ$) (Fernández-Jiménez and Palomo 2003). It is observed the presence of some minor crystalline compounds such as quartz (SiO_2) and mullite and magnetite (Fernández-Jiménez and Palomo 2003, Fernández-Jimenez, de la Torre et al. 2006).

Figure 4.4.1 XRD patterns for the starting materials Legend: A: alite 031-0301; Al: C_3A 032-1048; B: belite 049-1673; C: Lime CaO , 037-1497; F: ferrite phase 030-0226; Q: quartz 046-1045; M: mullite 084-1205; G: $CaSO_4 \cdot 2H_2O$ 037-1496; H: magnetite, Fe_2O_3 033-0664.

4.4.2 XRD analysis by Rietveld

The Rietveld-refined XRD pattern for all the starting materials are reproduced in Fig.4.4.2-5 (30% corundum was used as a standard.). The quantification findings are given in Table 4.4.1.

The reference OPC contains 86.7% clinker, 3.16% gypsum, 4.48% basanite and a little content of amorphous, 5.63%. The clinker content in the pre-industrial hybrid cement HYC appeared to be slightly higher than stipulated (on the order of 32.6 % rather than the 30 % specified).The activator content was nearly 4%.

The amorphous content was 54.5% which mainly come from the amorphous phase in slag and fly ash in the starting material.

In the pre-industrial hybrid cement HYP, the mineralogical composition obtained by rietveld analysis is 37.5% content which related to the crystalline phase of clinker. It appeared lower content of clinker, higher content of fly ash and also lower content of activator (46% clinker, 59.8% fly ash and 1.6% activator) when compared to the original objective, which could be due to two reasons:

- Some clinker phase has lower crystallinity and exits of part of amorphous phase when the clinker was produced at 1350 °C (Sánchez-Herrero 2017).
- The problem of dosage process of fabrication

In any case, this is the final pre-industrial hybrid cement materials used to investigate in this Ph.D. work.

Table 4.4.1 Rietveld quantification of cement mineralogy (using 30 % corundum as a standard).

Rietveld (%)	OPC		HYC		HYP		Fly ash
	%	Sub- Total	%	Sub- Total	%	Sub- Total	%
C ₃ S	50.0		20.05		8.10		
C ₂ S	21.9		5.45		24.0		
C ₃ A	9.29	86.7	3.98	32.5	1.30	37.5	
C ₄ AF	5.53		3.02		3.00		
C ₁₂ A ₇	/		/		1.10		
Gypsum(CaSO ₄ ·2H ₂ O)	3.16		/		1.20		
Basanite(CaSO ₄ ·1/2H ₂ O)	4.48		/		/		
Activator(Na ₂ SO ₄)	/		3.75		1.60		
Quartz	/		3.00		4.00		6.30
Mullite	/		6.27		3.80		11.7
Maghemite	/		/		/		1.10
Amorphous / Vitreous	5.63		54.5		52.0		80.6

The rietveld plot for initial fly ash presents a pattern (halo) typical of vitreous materials at 2 Θ angles of between 20 and 30°. The signals corresponding to the

crystalline phases found in the material, quartz, mullite and Fe_2O_3 in the form of magnetite, can also be seen in these diffractograms.

Figure 4.4.2 Rietveld quantification of the cement OPC studied using 30 % corundum as a standard.

Figure 4.4.3 Rietveld quantification of the cement HYC studied using 30 % corundum as a standard.

Figure 4.4.4 Rietveld quantification of the cement HYP studied using 30 % corundum as a standard.

Figure 4.4.5 Rietveld quantification of the cement FA studied using 30 % corundum as a standard.

4.4.3 MAS NMR analysis

Different from the XRD technique, solid state nuclear magnetic resonance does not depend on the presence of long-range atomic periodicity in a structure, but is sensitive to short and medium geometries with a certain order. Therefore, it is particularly useful for the investigation and characterization of amorphous phases such as glasses phases.

4.4.3.1 ^{29}Si MAS-NMR

The ^{29}Si MAS-NMR spectrum of the different raw materials as well their deconvolution spectra are shown in Fig.4.4.6. The Table 4.4.2 gives the information of the signals position and the area.

OPC: Fig.4.4.6 presents the ^{29}Si MAS-NMR spectrum of Portland cement. Sharp and symmetrical signals at -71.5 ppm, as well, a shoulder centred at around -73 ppm were obtained. The narrowest signal (-71.5 ppm) was attributed to belite ($\text{C}_2\text{S}_{\text{ss}}$) and the shoulder to alite ($\text{C}_3\text{S}_{\text{ss}}$) components, which are typical constituents of OPC clinker. After deconvolution, three signals were detected at -70.2, -71.5, and -73.4 (Q^0) ppm which assigned to the clinker contents (see Table 4.4.2).

HYC: The ^{29}Si MAS-NMR spectrum for the anhydrous cement exhibited a narrow, symmetrical signal centred over -71.6 ppm and three shoulders, one at around -69 ppm and the other two at around -73 and -74 ppm, denoting monomers (Q^0). The narrowest signal (-71.6 ppm) was attributed to belite ($\text{C}_2\text{S}_{\text{ss}}$) and the shoulder at -69 and -73 ppm was related to alite ($\text{C}_3\text{S}_{\text{ss}}$) components. Alite and belite are the two main constituents of Portland clinker. After spectrum deconvolution, a series of wide signals detected in addition to the aforementioned bands were assigned to the vitreous phase of the slag (see signals around -66.3, -74.3 and -77.6 ppm in Table 4.4.2). The lowest intensity signal centred at around -107 ppm, along with the signal at -89 ppm, were associated with components in the fly ash.

HYP: The ^{29}Si spectrum for the anhydrous cement gave a typical narrow peak at -71.7 ppm which was related to belite ($\text{C}_2\text{S}_{\text{ss}}$) in clinker. The lowest intensity signal centred at around -108 ppm, were associated with components in the fly ash. After spectrum deconvolution, the peak at -74.1 ppm could be related to alite ($\text{C}_3\text{S}_{\text{ss}}$) component in clinker. And two wide signals detected (at -89.5 and -107.2

ppm) which assigned to the glassy component of fly ash in this hybrid cement (Fernández-Jiménez, Puertas et al. 2003).

FA: The data obtained by application of ^{29}Si MAS-NMR spectrum to original fly ash are also presented in the Fig.4.4.6. The general ^{29}Si spectral of the fly ash gives a very wide asymmetric signal formed by several components (Fernández-Jiménez and Palomo 2003). The deconvolution spectrum gives us a series of wide signals, which are assigned to the components. The peaks appearing about -84.3, -93.6, -98.6, -103.4 and -108 ppm are assigned to the glassy component of the fly ash (Engelhardt and Michel 1987, Gomes and François 2000, Xie and Xi 2001). The peak at -88.1 ppm corresponds to the crystalline mullite phases presented in the ash, and the peaks at values of over -108 ppm are attributed to the presence of different crystalline phases of quartz; see Table 4.4.2 (Fernández-Jiménez and Palomo 2005).

Table 4.4.2 Deconvolution of ^{27}Al MAS-NMR spectra, signal position and area.

Materials	OPC		HYC		HYP		FAN	
Assignment	ppm	A(%)	ppm	A(%)	ppm	A(%)	ppm	A(%)
Slag			-66.3	3.72				
Alite	-70.2	25.52	-69.8	8.67				
Belite	-71.5	20.81	-71.6	11.3	-71.7	23.62		
Alite	-73.4	53.67	-73.0	8.45	-74.1	12.86		
Slag			-74.3	8.50				
Slag			-77.6	26.1				
Fly ash							-84.3	4.64
			-89.0	8.03	-89.5	10.31	-88.1	9.04
							-93.6	17.35
							-98.3	19.79
							-103.2	21.47
			-107.0	25.1	-107.2	53.21	-108.5	23.39
							-116.0	4.34

Figure 4.4.6 ^{29}Si MAS-NMR spectra and deconvolution spectra of OPC, HYC HYP and Fly ash.

4.4.3.2 ^{27}Al MAS-NMR

The ^{27}Al MAS-NMR spectrum of the different raw materials as well their deconvolution spectra are shown in Fig.4.4.7. The Table 4.4.3 gives the information of the signals position and the area after deconvolution.

OPC: It is observed that the signal has centered around + 80 ppm associated with tetrahedral aluminum (Al_T) of C_3A and C_4AF of clinker (Schneider, Cincotto et al. 2001, Andersen, Jakobsen et al. 2003). The signal at +72 and + 58 ppm (Table 4.4.3) are contribute to tetrahedral aluminum of clinker. The small signal appeared at +9.76 ppm and +3.32 ppm could be due to the formation of some metastable calcium aluminate hydrate due to probably the weathering of OPC.

HYC: The aluminium spectrum for the anhydrous cement HYC contained a wide asymmetrical signal centred on +60 ppm with a shoulder at +80 ppm. The former was attributed to overlapping signals (+60.15 and +41.17 ppm, see Table 4.4.3) of the Al_T present in the slag and fly ash (Fernández-Jiménez, Puertas et al. 2003, Garcia-Lodeiro, Fernandez-Jimenez et al. 2013) and the latter shoulder (+79.90 ppm) to the Al_T in the clinker. There are two small signal related to Al_O which has been observed. The signal at +10.1 ppm could be associated to little content of metastable calcium aluminate hydrate which come from clinker meteorization and the signal at +0.96 ppm properly related to the presence of mullite from fly ash (Qu, Martin et al. 2016).

HYP: The signal appears around +79 ppm (deconvoluted peak is +79.8 ppm) was related to the Al_T in the clinker and the other signals around +67.02 and 47.05 ppm were for Al_T in fly ash. A low intense signal was recorded around +1.55 and -5.27 ppm was attributed to Al_O in fly ash of starting material (Sánchez Herero M.J., Thesis, 2016).

FA: The results given in Fig. 4.4.7 for the ^{27}Al MAS NMR spectra clearly show that the initial present two wide components: one centered at + 53 ppm (with two deconvoluted peaks: + 54.66 and 42.9 ppm), associated with tetrahedral aluminium (Al_T) in fly ash, and another smaller signal at around + 2.5 ppm associated with octahedral aluminium (Al_O). The strong resonance at + 53/54 ppm is indicative of the existence of a majority of AlO_4 as opposed to AlO_6 units. In other words, it evidences the existence of -Si-O-Al- bonds (Fernández-Jimenez, de la Torre et al. 2006). The octahedral component is attributed to the aluminium in the mullite present in the ash.

Figure 4.4.7 ^{27}Al MAS-NMR spectra and deconvolution spectra of OPC, HYC, HYP and Fly ash.

Table 4.4.3 Deconvolution of ^{27}Al MAS-NMR spectra, signal position and area.

Materials		OPC		HYC		HYP		FAN	
Assignment		ppm	A(%)	ppm	A(%)	ppm	A(%)	ppm	A(%)
Al_T	Clinker	80.40	49.5	79.90	13.9	79.80	20.6	54.66	79.6
	Clinker	72.00	29.1						
	Clinker	58.00	12.0						
	Fly ash + slag / Fly ash			60.15	58.9	61.02	31.1		
Al_O				41.17	20.6	47.05	40.0	42.90	15.8
	Hydrate	9.76	2.91	10.10	1.41				
	Phases	3.32	6.52						
	Fly ash			0.96	5.29	1.55 -5.27	4.10 4.20	1.91	4.60

5 Effect of pre-curing temperature on the manufacture of cement paste

5.1 Introduction

Temperature is a key variable affecting the curing of cement-based materials, because it has strong influence in both the early hydration kinetics and the properties of the hardened paste or concrete. Proper curing of concrete plays important role on obtaining design strength and maximum durability.

The evaluated temperature leads to initial fast hydration which causes rapid precipitation of hydration products during the first hours and days. This is responsible for the early strength development ([Escalante-García and Sharp 1998](#)).

In this chapter, the study aimed to determine the physical-mechanical, mineralogical and microstructural properties of all the materials. The effect of the initial curing temperature (25 ± 1 or 85°C for 20 h) on hydration kinetics and the development of compressive strength were also explored. The hydration products formed were characterised using XRD, SEM/EDX and ^{27}Al and ^{29}Si MAS-NMR. This study also aimed to choose the suitable cement paste for further research of high temperature resistance.

5.2 Mechanical characterization

5.2.1 The mechanical strength of mortar

Fig.5.2.1 shows the 3-, 28- and 90 day compressive strength for the (4x4x16 cm) prismatic mortar specimens pre-cured at 25°C or 85°C within initial twenty hours. The liquid / solid, sand / cement ratios were listed in Table 3.2.1. Experiments condition was described in section 3.2.

Compressive strength clearly rose with time for all materials at both temperatures. The alkali-activated fly ash mortars could not harden at room temperature, the results was recorded as no data.

Initial pre-curing at the higher temperature (85°C) improved 3 day strength substantially, which clearly exhibited in plot of OPC, and hybrid cements HYP and HYP. That effect declined in more mature specimens. The 28 day strength of three cements pre-cured at 85°C is very close to the strength pre-cured at 25°C . For three cement mortars pre-cured at ambient temperature, from 28 days until 90 days, the compressive strength showed better behaviour.

Figure 5.2.1 Compressive strength of OPC, HYC, HYP and FAN (pre-cured at 85 °C) in mortar by testing time and two pre-curing temperature

The compressive strength of OPC (in Fig.5.2.1) shows that in 3 days, the mechanical strength of OPC pre-cured at 25 °C reached 30 MPa. Initial pre-curing at the higher temperature improved 3-day strength from 30 to 47 MPa. However, the 28-day and 90-day strength of the cement pre-cured at 25 and 85 °C exhibited quite close values (55 MPa in 28 days and 58 MPa in 90 days).

One of industrial hybrid cement (HYC) used was manufactured at Latin-American cement plant (about 20 tons were manufacture). The standards are different according to the area. In some Latin-American countries as Venezuela, Mexico, Colombia the standards are more similar to ASTM than the EN standards. In Colombia, the performance specification for hydraulic cement, standard NTC 121 (equivalent to ASTM C1157/C1157M.11 (11 2011)), was approved in 2014. This standard classifies cement types by their features and performance. The minimum 3-, 7- and 28-day compressive strength values required for general purpose hydraulic cement (UG) are 8, 15 and 24 MPa, respectively (NTC 121). Similar specifications about the specimens manufacture and compressive strength values are in Venezuela standards (COVENIN 484-89

(484-89 1989) and COVENIN 28-93 (28-93 1993)) or Mexico standards (NMX-C-061-ONNCCE-2010 NMX-C-414-ONNCCE-2016 (NMX-C-061-ONNCCE-2010 2013, NMX-C-414-ONNCCE-2016 2016)).

In some Latin-American country as Colombian standard NTC 220 stipulates the use of 5-cm cubic specimens (with a cement/sand ratio of 1/2.75, the amount of mixing water should be one that produces a flow of 110 ± 5 in 25 strokes with the flow table) to determine mechanical strength. In the present study, however, prismatic ($4 \times 4 \times 16$ cm) mortar specimens were prepared as per standard EN 196-1 (water/cement ratio = 0.5; sand/cement = 3/1), which is nearly equivalent to standards ASTM C348 and NTC 120.

With the strength values recorded (despite the use of $4 \times 4 \times 16$ instead of 5 cm cubic specimens, see Fig. 5.2.1 **HYC**), the hybrid cement **HYC** developed compressive strength high enough to be regarded as apt for general construction in some country as cement type UG in Colombia, further to national standard NTC 121. From the standpoint of its mechanical strength, it could also be classified as Type 32.5 cement under European legislation. Nonetheless, given its low clinker content, according to standard EN 196-1, it would have to be classed as a Type V cement.

The other hybrids cement (**HYP**, with 50 % belite clinker, only 8.1% content of C_3S) exhibited lower compressive strength (10 MPa) in 3 days when pre-cured at ambient temperature. The 28-day strength of the cement pre-cured at 25 °C was 32 MPa, while the 90-day value was 42 MPa. In contrast, the specimens pre-cured at 85 °C exhibited 3-day compressive strength of 30 MPa, thereafter the value remained flat, without obvious rise. The strength values recorded of **HYP** after 28 days were similar to **HYC**. It would also be classified as Type 32.5 cement as well.

Alkali-activated cement **FAN** showed strength value of 40 MPa in 3 days, higher than **OPC**, **HYC** and **HYP**. The strength of this type of binder material is quite influenced by characteristic of raw materials, activators, curing conditions (Fernández-Jiménez and Palomo 2003). It reached a relatively high mechanical strength value in early age. The 28-day and 90-day compressive strength exhibited a slightly rise until 50 MPa. For this material, the activation needs pre-curing high temperature according to the fact that it did not harden at room temperature.

5.2.2 The mechanical strength of Paste

Figure 5.2.2 Compressive strength of OPC, HYC, HYP and FAN (Pre-cured at 85 °C) in paste by testing time and two pre-curing temperature.

Fig.5.2.2 gives the 3-, 28- and 90 day compressive strength for the (1x1x6 cm) prismatic paste specimens pre-cured at 25 °C or 85 °C. The water / cement, ratio was listed in Table 3.2.1. The elaboration details of specimens and the pre-curing condition process were introduced in section 3.1.1.1.

The mechanical behaviour for pastes is quite similar to mortars. The evaluated pre-curing temperature led to fast early hydration, which confirmed by the improving of 3 days compressive strength of the three cements (OPC, HYC and HYP) pastes. Then the influence of high pre-curing temperature declined on the older pastes. After 28 days pastes pre-cured at 25 °C exhibited better mechanical strength.

Alkali-activated fly ash pastes were not hard at room temperature (25°C), however when this material were pre-cured at 85 °C in initial 20 hours, the early strength (three day) has already reached almost 30 Mpa. With the hydration time, the compressive strength of alkaline activated fly ash (AAFA) pastes has shown

a clear stability. It indicates that AAFA bind materials, in early time, it will be reach acceptable mechanical values.

5.2.3 Effect of temperature on mechanical characterization

It has been studied that increased temperature promotes the hydration to high early strength. However, later when compared to the cements hydrated at room temperature, the strength of cements hydrated at increased temperature is reduced (Price 1951, Escalante-García and Sharp 2001, Lothenbach, Winnefeld et al. 2007). The reason is curing at a higher temperature, for instance, is known to expedite initial OPC hydration. The C-S-H gel (main hydration products) formed during OPC hydration at temperatures $> 65\text{ }^{\circ}\text{C}$ is more highly polymerized (Garcia-Lodeiro, Fernandez-Jimenez et al. 2013, Donatello, Maltseva et al. 2014, Alahrache, Winnefeld et al. 2016). Although rapid hydration at evaluated temperature gains the early strength, the final strength is lower. In this work, the results of OPC also confirm the former study even the curing condition is distinct to the reference.

In hybrid cements, blast furnace slag, and fly ash were used as supplementary materials. Temperature effect on the two types of alkaline cements should be considered distinguish. a) In the alkaline activation of blast furnace slag (AABFS), temperature hastens initial strength development (as in OPC), although strength declines at more mature ages (Wang, Scrivener et al. 1994, Fernández-Jiménez, Palomo et al. 1999, Bernal, Mejía de Gutiérrez et al. 2012). The C-A-S-H gel formed, as well as the secondary reaction products, is more crystalline than when heat is not applied. b) In the alkaline activation of fly ash (AAFA), curing temperature (between 65 and $90\text{ }^{\circ}\text{C}$) plays a very important role, as heat accelerates early age reactions, with the product exhibiting 1-day mechanical strength upward of 30MPa , meanwhile this binder material once it hydrated in early time, the mechanical strength performed more stable than OPC (Fernández-Jiménez, Palomo et al. 1999, Palomo, Alonso et al. 2004).

It is clearly obtained the behaviour that pre-curing temperature influences the early mechanical strength dramatically from three-day compressive data of mortar and pastes. Hybrid cements has different composition, however similar mechanical behaviour of OPC, the discussion is below.

Pre-cured at $25\text{ }^{\circ}\text{C}$ (ambient temperature)

When the cements hydrated at room temperature, OPC has best mechanical behaviour at 3 days, and then followed by HYC and HYP; alkaline activated fly

ash did not harden at room temperature. In Fig.5.2.3, 3 days compressive of mortars and pastes pre-cured 25 °C and the C₃S quantification content were plotted. The quantification data come from the Rietveld-refined XRD pattern (see Table 5.4.1) analysis. The trends clearly showed the relation between C₃S and early compressive strength. The two hybrid cements exhibited lower 3 days compressive strength due to lower C₃S.

Figure 5.2.3 Plot of 3-day compressive strength of mortars and pastes pre-cured at 25°C versus C₃S quantification content (data from Rietveld-refined XRD).

Pre-cured at 85 °C (high temperature)

The temperature 85 °C is agreed with many researcher (Fernández-Jiménez, Palomo et al. 1999, Palomo, Grutzeck et al. 1999, Kovalchuk, Fernández-Jiménez et al. 2007) can increase times of velocity of mechanical strength for AAFA. This is due to high temperature improve the dissolution of the raw fly ash materials. At the same time, elevated temperature also accelerated OPC hydration. It could be discussed the effect of high pre-curing temperature on studied materials according to the various component of raw materials.

The influence trends of higher temperature was calculated and listed in Table 5.2.1, which considering the compressive value pre-cured at ambient temperature (25 °C) as base data (see Formula 4.1). In the table plus “+” means increase of trends and minus “-” means decrease of trends.

$$\text{Inf.} = \frac{\text{COM}_{85^{\circ}\text{C}} - \text{COM}_{25^{\circ}\text{C}}}{\text{COM}_{25^{\circ}\text{C}}} \times 100\% \quad (5.2.1)$$

Among three cementitious materials, the temperature has relatively large influence on HYP, and smaller influence on OPC. However, the mechanical behaviour has been related to the hydration process, it contains complexity. It could be qualitative analyzed and related to the composition of the raw materials, especially the contents of fly ash. High temperature accelerates early age reactions of fly ash extremely, which also could be proved by the material fly ash Lada, the mortar activated with NaOH solution at 25 °C did not harden, however when it was pre-cured at 85 °C, the 3 day strength has reached 42 Mpa.

Table 5.2.1 The Information of pre-curing temperature at 85 °C, considered the strength at 25 °C as the standard.

	OPC (%)	HYC (%)	HYP (%)	FA
Fly ash content (design) %	0	~ 35	~ 47	100
3D	+55	+85	+231	+
28D	-2	-12	-0.9	+
90D	-1	-11	-20	+

From the mechanical behaviour, it illustrated that the two hybrid cements studied in this thesis exhibited similar behaviour like the reference material OPC under the influence of high pre-curing temperature. The results proved that, although the early compressive strength of hybrid cement is low, the mature age mechanical strength pre-cured at ambient temperature (25 °C) is better.

5.3 Reaction Kinetics

Conduction calorimetry, as a technique for studying the kinetics of chemical reactions, has always played important role in the interpretation of mechanisms that govern Portland cement hydration. Furthermore, fuller understanding of the effects of supplementary cementitious materials on hydration has been contributed to this technique, it was deemed to be able likewise contribute significant to the understanding of different system of hybrid cements.

5.3.1 OPC

The calorimetric curves for the reference OPC paste are plotted in the Fig.5.3.1 for pre-curing temperatures of 25 and 85 °C. These curves followed a pattern characteristic of hydration curves for modern Portland cement. Pre-induction occurred too quickly for the respective peaks to be visible on these curves.

Figure 5.3.1 Heat flow and total heat released by OPC pre-cured at 25 or 85 °C

At 25 °C, after a short induction period, the main peak at 6.25 h with a heat flow of 14.5 J/g h was observed in the acceleration period was associated with the reaction of Alite (C_3S). Typical shoulder peaks around 10 h and 20 h which following the main peak in the deceleration period appeared, which related to the renewed dissolution of C_3A with formation of ettringite and the formation of AFm phase from C_3A and ettringite (Bullard, Jennings et al. 2011, Deschner,

Winnefeld et al. 2012). High pre-curing temperature accelerated the hydration rate of cement dramatically; at 85 °C the main peak related to Alite reaction was recorded at 1.53 h with a clearly higher heat flow of 677 J/g h.

It is from the Fig.5.3.1 that, when the curing temperature increased, the width of main hydration peak decreased and the peak became more symmetrical and steeper. It indicates that the hydration rate is higher at evaluated curing temperature. At the same time, the first typical shoulder peak where a secondary formation of ettringite occurs at 25 °C was not observed at 85 °C, which due to the absence of ettringite formation at high curing temperature. The subsequent broad peak around 6h is maybe an overlap peak corresponding to the dissolution of C_3A and the formation of AFm phase from C_3A . An obvious fact can be indicated that higher pre-curing temperature fastens early hydration and products precipitation (the main peak is 6.25 hours at 25 °C and 1.53 hours at 85 °C)

5.3.2 HYC

The heat flow (J/g h) and total heat released (J/g) during pre-industrial hybrid cement, HYC hydration are plotted in Fig.5.3.2 for pre-curing temperatures of 25 and 85 °C. A comparison of the heat output rate profiles reveals that both temperatures have profiles similar to that of a normal OPC and so similar terminology is used in their interpretation here. Pre-induction occurred too quickly for the respective peaks to be visible on these curves.

At 25 °C, the acceleration-deceleration curve observed after a short induction period, with a peak at 10.8 h, was associated with the precipitation of reaction products (Escalante-Garcia and Sharp 2000, Garcia-Lodeiro, Fernandez-Jimenez et al. 2013, Donatello, Maltseva et al. 2014). The rounded form of the band suggested a series of overlapping reactions (clinker hydration and slag and fly ash activation). These reactions induced fairly low heat of reaction, around 200 J/h. A higher pre-curing temperature expedited the hydration rate of cement considerably: at 85 °C the main band peaked at 2.2 h with a heat flow of 225 J/g h and clearly greater heat intensity.

It is clear from Fig.5.3.2 that, with increasing temperature, the maximum hydration peak increases, while the time to reach the peak decreases. Additionally, it is observed that the peak width decreases with increasing temperature, indicating a faster hydration rate with time. This means, that the rate of cement and the SCMs hydration is accelerated with temperature,

consistent with the laws of chemical kinetics and may also explain the maximum total heat plateau occurring faster with temperature. It can also be observed in Fig.5.3.2 that the accumulated total heat increases with temperature, it is probably due to more hydration products at early age are precipitated.

Figure 5.3.2 Heat flow and total heat released by HYC pre-cured at 25 and 85 °C

5.3.3 HYP

Fig.5.3.3 exhibited the heat flow (J/g h) and total heat released (J/g) during pre-industrial hybrid cement, HYP, hydration for pre-curing temperatures of 25 and 85 °C. Pre-induction occurred too quickly for the respective peaks to be visible on these curves. The heat output rate profiles reveal similar profiles at both temperatures. The water-hydrated of HYP generated a different heat flow curve from OPC.

At 25°C, in this material, a signal with two peaks at 4.9 and 8.9 h appeared. The first peak ($t = 6.41$ h), normally associated with the precipitation of reaction products, the rounded form of the band suggested a series of overlapping reactions (clinker (C_3S) hydration and fly ash activation). These reactions induced fairly low heat of reaction, around 130 J/h. This reaction was more intense and lower in height than the OPC profile because of the lower content of C_3S (8.1 %). The second peak ($t=8.89$ h) can be explained by the precipitation of ettringite and fly ash activation. The cumulative heat curves of the two materials exhibited behaviour similar. But the cumulative heat value of HYP was almost half of OPC, which can be explained by the high content of fly ash, according to the reference, the amount of cement available especially of C_3S content was smaller in the HYP (48 % belite clinker with 8.1 % of C_3S) than in the OPC, and also smaller than HYC (20 % of C_3S) (Lothenbach, Scrivener et al. 2011, Berodier and Scrivener 2015).

At 85°C, a quick peak was recorded in pre-induction period associated with the dissolution. The acceleration-deceleration curve observed after induction period, with two peaks at 3.5 and 4.6h, the first main band was related to clinker (C_3S) hydration and the second band was a series of overlapping reactions which could be explained by the reaction of C_3A and fly ash activation.

From Fig.5.3.3 it is clear that with increasing temperature, the hydration peak increases and much more in the second peak, while the time to reach the peak decreases. Additionally, it is observed that the peak width decreases with increasing temperature, indicating a faster hydration rate with time. This means, that the rate of cement and the SCMs hydration is accelerated with temperature, consistent with the laws of chemical kinetics and may also explain the maximum total heat plateau occurring faster with temperature. The accumulated total heat was much higher at 85 °C than 25 °C, it should be due to more hydration products at early age are precipitated.

Figure 5.3.3 Heat flow and total heat released by HYP pre-cured at 25 or 85°C

5.3.4 FAN

Fig.5.3.4 depicts the heat release response of 8 M NaOH activated fly ash. At 85 °C, the initial disilusion peak of FAN is high and appear fast, it maybe because the higher alkalinity with the function of activator. The process of dissolution of fly ash in a highly alkaline solution begins with the breakdown of the covalent Si-O-Si and Al-O-Al bonds in the glassy phase of fly ash and the release of these ions into the pore solution(Chithiraputhiran and Neithalath 2013). The secondary acceleration peak appeared in FAN, It happened around 9 hours with cumulative heat around 400 J/g, earlier the peak was narrower which related to the fact that formation of reaction products (N-A-S-H gel) is faster.

Figure 5.3.4 Heat flow and total heat released of FAN pastes at 85 °C

5.4 Mineralogical and microstructure characterization

5.4.1 XRD results

5.4.1.1 OPC

In Fig.5.4.1, the patterns for anhydrous OPC and its hydrated paste of 3, 28 and 90 days with the initial pre-curing (25 and 85 °C) are presented. Table 5.4.1 lists the ICDD cards used to identify each phase.

Figure 5.4.1 XRD patterns for OPC pre-cured at different temperatures.

Legend:

- A: Alite, C_3S ;
- Al: C_3A ;
- B: Larnite, C_2S ;
- C: Calcite $CaCO_3$;
- E: Ettringite, $C_6\bar{A}\bar{S}_3H_{32}$;
- F: Bronnillerite, $Ca(Al, Fe+3)_2O_5$;
- P: Portlandite, $Ca(OH)_2$;
- G: Gypsum, $CaSO_4 \cdot 2H_2O$
- α : Hemicarboaluminate, $C_3A \cdot Ca[OH \cdot (CO_3)_{0.5}] \cdot H_{11.5}$;
- β : Monocarboaluminate, $C_3A \cdot CaCO_3 \cdot H_{11}$

Table 5.4.1 ICDD card used to identify the mineralogical phases present in XRD.

Mineralogical phase	PDF No.
Alite	031-0301
Belite/Larnite	032-1048
Calcium Aluminate	033-0302
Calcite	083-0578
Ettringite	041-1451
Bronnillerite	030-0226
Portlandite	044-0226
Gypsum	037-1496
Hemicarboaluminate	041-0221
Monocarboaluminate	041-0219

The OPC presents the peaks associated with the typical clinker phases (alite, belite, calcium aluminates and ferrite phase) and gypsum. The peaks associated to the anhydrous phases of the clinker decreased in intensity as the hydration time increased. As a new crystalline phase, the presence of portlandite is detected, whose intensity increases as a function of the hydration time. The presence of calcite is also detected in both cases. And the halo between 20-35 °C is associated to the formation of C-S-H gel.

One distinguish obtained is that ettringite is only detected in samples pre-cured at room temperature, in the pre-cured at 85 °C (during the first 20 hours), after 90 days the presence of ettringite is still undetected in the samples pre-cured at 85 °C.

The other difference between the samples pre-cured at different temperature from the XRD traces was the type of carboaluminate formed. At 25 °C, after 28 days, monocarboaluminate was formed (in Fig.5.4.1, colourful marked) and stilled detected at mature ages. Monocarboaluminate is stable at 25 °C, the reason is carbonate provides thermodynamic stabilization for AFm phase (Matschei, Lothenbach et al. 2007). At 85 °C, after 3 days, in all the samples, hemicarboaluminate were detected. The strongest intensity of this phase appeared in the 3-day sample, after 28 days, the signal related to the hemicarboaluminate were detected, however, the intensity is very weak in the original XRD data, which indicated that this carboaluminate was metastable. It was reported by T. Matschei et al. (2007), as an additional AFm phase of OPC hydration; hemicarboaluminate is not stable at 25 °C in the presence of excess calcite.

Figure 5.4.2 Representation of XRD peak intensity corresponding to portlandite ($2\theta = 18.04^\circ$) of OPC at different pre-curing temperature with time.

In Fig.5.4.2, the peak intensity of XRD patterns which corresponded to $\text{Ca}(\text{OH})_2$ and CaCO_3 was plotted. It should be aware of that the data is qualitative analysis, which only shows the trends of crystalline phases.

5.4.1.2 HYC

Figure 5.4.3 XRD patterns for HYC pre-cured at different temperatures.

Legends:

A: Alite, C_3S ;
 Al: C_3A ;
 B: Larnite, C_2S ;
 C: Calcite CaCO_3 ;
 E: Ettringite, $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$;
 F: Bronmillerite, $\text{Ca}(\text{Al}, \text{Fe}+3)_2\text{O}_5$;
 P: Portlandite, $\text{Ca}(\text{OH})_2$;
 Q: Quartz, SiO_2
 M: mullite;
 G: Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
 α : Hemicarboaluminate, $\text{C}_3\text{A} \cdot \text{Ca}[\text{OH} \cdot (\text{CO}_3)_{0.5}] \cdot \text{H}_{11.5}$;
 β : Monocarboaluminate, $\text{C}_3\text{A} \cdot \text{CaCO}_3 \cdot \text{H}_{32}$
 χ : U Phase, $\text{C}_4\text{A}\bar{\text{S}}_{1.5}\text{N}_{0.5}\text{H}_{15}$

Table 5.4.2 ICDD card used to identify the mineralogical phases present in XRD.

Mineralogical phase	PDF No.
Alite	031-0301
Belite/Larnite	032-1048
Calcium Aluminate	033-0302
Calcite	083-0578
Ettringite	041-1451
Bronmillerite	030-0226
Portlandite	044-0226
Quartz	046-1045
Mulitte	084-1205
Gypsum	037-1496
Hemicarboaluminate	041-0221
Monocarboaluminate	041-0219
U phase	044-0272

The Fig.5.4.3 exhibited XRD patterns for HYC pre-cured at different temperatures. An analysis of the variations in the diffractograms over time and by pre-curing temperature revealed the following:

In the 25 °C specimens, the intensity of the diffraction lines associated with clinker anhydrous phases declined over time. In contrast, the lines associated with the quartz and mullite present in the fly ash remained unaltered. The new crystalline phases detected included portlandite, ettringite, calcite and a very low intensity signal associated with hemicarboaluminates.

Rather than rising over time, the intensity of the portlandite signal declined between 28 and 90 days (see Fig.5.4.3 and Fig.5.4.4), this behaviour is different to OPC. It is an indication that the fly ash not initially activated exhibited pozzolanicity at more mature ages with consumption of $\text{Ca}(\text{OH})_2$ (Lothenbach, Scrivener et al. 2011, Schöler, Lothenbach et al. 2015). Intensity of calcite increased from 3 days to 90 days the same as OPC. With time, carbonation happened in the pastes. In Fig.5.4.4, pre-curing at 85 °C exhibited less portlandite and calcite intensity than at 25 °C.

Figure 5.4.4 Representation of XRD peak intensity corresponding to portlandite ($2\theta = 18.04^\circ$) and calcite ($2\theta = 29.0^\circ$) of HYC at different pre-curing temperature with time.

For pasted pre-cured at 85°C, the most prominent difference between these diffractograms and the patterns for the cement pre-cured at 25°C was the absence of ettringite, even after 90 days.

Meanwhile, diffraction lines associated with U phase were detected on the XRD traces for all the pastes hydrated with initial twenty hours at 85 °C (3, 28, and 90-day pastes), although the intensity were quite low, especially the 3-day samples. This phase ($\text{C}_4\text{A}\bar{\text{S}}_{1.5}\text{N}_{0.5}\text{H}_{15}$) is a calcium sulfoaluminate morphologically similar to calcium monosulfoaluminate ($\text{C}_4\text{A}\bar{\text{S}}\text{H}_{12}$), but with

sodium in its structure, which possessed a higher interlayer distance (Dosch and Zur Strassen 1967, Li, Le Bescop et al. 1996). According to the study of G. Li et al. the formation of U phase can occur only at high alkaline concentration, in the presence of sulfates and alumina, this compound is unlikely to form in traditional cement pastes (OPC pastes) because the particular formation condition are generally not satisfied.

All the diffractograms contained a hump (colour marked) from 25 to 35° which, as discussed below, was associated with the possible formation and precipitation of a mix of C-(A)-S-H/C-A-S-H gels. The precipitations of a mixture of gels have been demonstrated in previous works in blended cement (García-Lodeiro, Maltseva et al. 2012) and compatibility studies of synthetic gels (García-Lodeiro, Fernández-Jiménez et al. 2010, Garcia-Lodeiro, Palomo et al. 2011, Alahrache, Winnefeld et al. 2016).

5.4.1.3 HYP

In Fig.5.4.5, the patterns for anhydrous hybrid cement HYP and its hydrated paste of 3, 28 and 90 days with the initial pre-curing (25 and 85 °C) are exhibited.

The anhydrous HYP spectrum presents the peaks associated with clinker phases of alite, belite calcium aluminates and ferrite. Peaks associated with mullite and quartz was detected. These phases are typical from fly ash content in the raw material.

After the cement hydrated, the lines related to the quartz and mullite present in the fly ash remained unaltered in samples at different pre-curing temperature. The intensity of the diffraction lines associated with clinker anhydrous phase declines with time, and there were no obvious portlandite signals which were detected after HYP hydration even at three days of samples. The intensity of portlandite related peak ($2\theta = 18.04^\circ$) is very small but still be used here to compare the results. Calcite as new crystalline phase was also obtained in XRD patterns of pastes. The intensity of calcite was influenced by pre-curing temperature in the pastes tested at 28 and 90 days.

Figure 5.4.5 XRD patterns for HYP pre-cured at different temperatures.

Legends:

A: Alite, C_3S ;

Al: C_3A ;

B: Larnite, C_2S ;

C: Calcite $CaCO_3$;

E: Ettringite, $C_6\bar{A}\bar{S}_3H_{32}$;

F: Bronmillerite,

$Ca(Al, Fe+3)_2O_5$;

Q: Quartz, SiO_2

M: mullite;

G: Gypsum, $CaSO_4 \cdot 2H_2O$

α : Hemicarboaluminate,
 $C_3A \cdot Ca[OH \cdot (CO_3)_{0.5}] \cdot 11.5H_2O$;

β : Monocarboaluminate,

$C_3A \cdot CaCO_3 \cdot 32H_2O$

χ : U-Phase, $C_4\bar{A}\bar{S}_{1.5}N_{0.5}H_{15}$

Table 5.4.3 ICDD card used to identify the mineralogical phases present in XRD.

Mineralogical phase	PDF No.
Alite	031-0301
Belite/Larnite	032-1048
Calcium Aluminate	033-0302
Calcite	083-0578
Ettringite	041-1451
Bronmillerite	030-0226
Quartz	046-1045
Mullite	084-1205
Gypsum	037-1496
Hemicarboaluminate	041-0221
Monocarboaluminate	041-0219
U phase	044-0272

For the pastes pre-cured at 25 °C, ettringite was formed in all age samples. Carboaluminate ($C_3A \cdot Ca[OH \cdot (CO_3)_{0.5}] \cdot 11.5H_2O$), as a new phase was detected in 3-day samples, but not appeared in mature pastes. The reason is that these phases are metastable. With time they probably transformed to calcite.

In the 85 °C specimens, ettringite disappeared. Clearly diffraction lines appeared which were identified as U-phase. This behaviour is similar to that observed in

HYC pastes. The intensity of U-phase clearly declined in 90 days pastes, which indicated that this phase maybe transformed to other phases.

From Fig.5.4.6, we can see that when samples pre-cured at 85 °C, less calcite and portlandite were detected by XRD in HYP paste. It could be due to high pre-curing temperature contributed to more pozzolanic reaction with more consume of Ca(OH)_2 than at 25 °C, which improved 3-days mechanical strength.

Figure 5.4.6 Representation of XRD peak intensity corresponding to portlandite ($2\theta = 18.04^\circ$) and calcite ($2\theta = 29.0^\circ$) of HYP at different pre-curing temperature with time

According to the fact that FAN binder material don't harden at room temperature, only alkaline-activated fly ash paste pre-cured at 85 °C (20 hours initially) were studied by XRD at different ages. Fig.5.4.7 gives XRD spectra. For original ash, the majority vitreous phase come from original ash was related to the hump from $20-30^\circ$ 2θ . A number of minority phase crystalline phases: mullite, quartz and magnetite and some CaO were detected.

When the fly ash is activated by sodium hydroxide (8 M NaOH) according to the previously mentioned conditions, the main reaction product is that already mentioned alkaline aluminosilicate gel, also named N-A-S-H gel with lower crystalline structure (Palomo, Grutzeck et al. 1999, Palomo, Alonso et al. 2004). This gel does not pattern but appears with low and scattered bands, which could be attributed to the halo from $18-38^\circ$ of 2θ . This hump, in XRD diffractogrammes overlaps partially with that of original ash; however it appears slightly shifted toward higher values (Fernández-Jiménez and Palomo 2005). The aluminosilicate gel can be regarded to be a zeolite precursor (Fernández-Jiménez and Palomo 2005, Criado, Fernández-Jiménez et al. 2007).

Figure 5.4.7 3, 28 and 90-day XRD patterns for FAN pre-cured at 85 °C.

legends:

C: Calcite, CaCO_3

H: Magnemite, Fe_2O_3

M: Mullite

Ch: Herschelite, $\text{NaAlSi}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$

n: hydroxysodalite, $\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$,

Q: quartz, SiO_2

I: lime, CaO

Table 5.4.4 ICDD card used to identify the mineralogical phases present in XRD.

Mineralogical phase	PDF No.
Calcite	083-0578
Magnemite	033-0664
Mullite	084-1205
Herschelite	088-1261
quartz	046-1045
hydroxysodalite	041-0009
lime	038-1429

The crystalline phases originally existing in the fly ash, quartz, mullite, etc, have not been apparently altered by the activation reactions. Some authors (Steenbruggen and Hollman 1998) reported that when mullite and quartz was submitted to strong alkaline medium, they are slightly alerted. In our case, the intensity of these phases maintained approximately equal in the samples corresponding to the activated fly ash in different testing age (3, 28 and 90 days).

However, one important data collected in XRD patterns for FAN pastes were noted is: some minor crystalline phases exist in the activated fly ash samples. All the tested samples present some intense peaks associated presence of zeolites like hydroxysodalite ($\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and especially herschelkite ($\text{NaAlSi}_2\text{O}_6 \cdot 3\text{H}_2\text{O}$). These crystalline phases are typical reaction products of AAFA systems (Fernández-Jiménez and Palomo 2005).

From the view of mineralogical point, the XRD patterns of alkaline activated fly ash of different tested age's samples exhibited quite similar.

5.4.2 ^{29}Si and ^{27}Al MAS NMR studies

In this section, ^{29}Si and ^{27}Al MAS NMR spectroscopy of selected pastes were studied to understand the nanostructure characterization. The deconvolution of the obtained spectra is used to make quantitative analysis, especially on the ^{29}Si NMR, which provides further information about the structure changes, chain lengths, and elements' ratios of reaction products. It should be paid attention that for complex blended systems (two hybrid cements HYC and HYP), the deconvolution of spectra could be more complex and difficult to identify each of them, however the study of MAS NMR data could offer valuable nanostructure information.

Therefore, for the aim of further analysis and studying of ^{29}Si and ^{27}Al MAS NMR spectra, the deconvolution was carried out by the program Origin 9.0 and Dmfit 2011. For the spectra with ignorable noises, Origin 9.0 was used to make deconvolution by Gaussian with a relation of L/G equals to 0.5. For the spectra with noises cannot be ignored (raw fly ash material), Dmfit 2011 was used to study the deconvolution, L/G ratio maintain between 0 and 0.8 depending every each single deconvoluted signals.

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5.4.2.1 OPC

The Fig.5.4.8 shows the ^{27}Al NMR-MAS spectra for the anhydrous cement and the 28-day pastes pre-cured at two temperatures of OPC.

Figure 5.4.8 ^{27}Al MAS-NMR spectra and the deconvolution spectra for anhydrous OPC of its 28-day pastes.

The ^{27}Al NMR-MAS Spectra for anhydrous cement had a wide asymmetrical signal at around 80 ppm which is basically associated with tetrahedral aluminium (Al_T) of C_3A and C_4AF in the clinker (Colombet and Grimmer 1994). This spectrum contains a very weak signal between 0-10 ppm, with two deconvolution peaks associated with hydrated cement phases, indicating that this cement may have been slightly weathered when the spectra were recorded.

When the cement was hydrated the intensity of the +80 ppm signal declined and almost disappeared, a low intense signal centred around +65 ppm appeared in both spectra which maybe contributed to the tetrahedral aluminium (Al_T) incorporated in the production of C-S-H gel (can be described as C-(A)-S-H gel) (Richardson and Groves 1993). The decline in Al_T signal indicates that the reactions taking place in the calcium aluminate in the clinker. Simultaneously a new, very intense signals associated with octahedral aluminium (Al_O) appeared at around 12-11 and 9-10 ppm. The signal at around +12 ppm was attributed to the Al_O in the ettringite-like phases. The deconvolution data of ^{27}Al MAS-NMR spectra was listed in Table 5.4.5. The signals at around +10/+9 ppm may be associated with the presence of a small amount of octahedral Al (Al_O) in AFm phases (Faucon, Charpentier et al. 1998, Andersen, Jakobsen et al. 2003, Andersen, Jakobsen et al. 2006).

Table 5.4.5 Deconvolution of ^{27}Al MAS-NMR spectra, showing signal position and area of OPC.

Sample	OPC	Al_T			Al_O		Al_T/Al_O
Anhyd.	Pos.(ppm)	80.40	72.00	58.00	9.76	3.32	
	Area (%)	49.05	29.10	12.00	2.91	6.52	9.6
25 °C	Pos.(ppm)	66.36		13.15	9.16	5.00	
	Area (%)	21.51		23.26	34.30	20.93	0.3
85 °C	Pos.(ppm)	65.15			9.83	5.00	
	Area (%)	17.09			64.53	18.38	0.2

In the deconvolution spectrum a poorly defined signal at lower values (+5 ppm) is initially considered to be due to the presence of Al in amorphous gibbsite-like phases (Skibsted, Henderson et al. 1993, Andersen, Jakobsen et al. 2006). This compound was called by them the third aluminate hydrate, abbreviated as TAH, which was claimed to be found in hydrated Portland cement. However, the low concentrations of this phase make it different to be identified.

Two signals appeared at round +13 ppm and +9.16 ppm spectrum for 28-day hydrated pastes pre-cured 25 °C. The signal at +13.15 ppm is related to the Al_O in ettringite. The other band centred at around +9.16 ppm attributed to the presence of AFm (Faucon, Charpentier et al. 1998, Andersen, Jakobsen et al. 2006). According to the XRD results, this signal is maybe associated here with the formation of monocarboaluminate ($C_3A \cdot CaCO_3 \cdot 11H_2O$).

When pre-curing temperature changed up to 85 °C in the beginning twenty hours, ²⁷Al MAS-NMR spectra for 28-day pastes exhibited distinct signals. The band at +13 ppm disappeared, and the peak at +9.16 ppm shifted to +9.83 ppm. This phenomenon could be explained combined with XRD results which confirmed the fact that there is no ettringite formed in the sample pre-cured at 85 °C and also different type of AFm phases were formed. The new signal at +9.8 ppm should be related here to the formation of hemicarboaluminate ($C_3A \cdot Ca[OH \cdot (CO_3)_{0.5}] \cdot 11.5H_2O$). Meanwhile, the low intensity signal around +65 ppm of hydrated pastes also shifted to less passive values (from +66.36 ppm to +65.15 ppm, see Table 5.4.5) at high pre-curing temperature, it indicates that more number of Al has cooperated in the C-S-H gel and to form C-(A)-S-H.

The assignation of each deconvoluted peaks of ²⁷Al MAS-NMR spectra are listed in the Table 5.4.6. Attention should be paid to the fact that some low intensity deconvoluted signals attributing to hydrate phases for anhydrate OPC were not come from the raw materials. The assignation of these peaks is explained as hydrate phases.

Table 5.4.6 ²⁷Al MAS-NMR deconvoluted peaks assignation.

Assignment	Chemical shift δ ppm		
	Anhydrate OPC	25 °C	85 °C
Clinker	80.0		
Clinker	72.0		
C-(A)-S-H		66.4	66.2
Hydrate Phases *	58.0		
$C_6\bar{A}\bar{S}_3H_{32}$		13.2	
$C_3A \cdot Ca[OH \cdot (CO_3)_{0.5}] \cdot 11.5H$			9.83
Hydrate Phases	9.76		
$C_3A \cdot CaCO_3 \cdot 11H$		9.16	
TAH		5.00	5.00
Hydrate Phase	3.32		

Hydrate Phase *: Here referred to the hydrate cement phases due to slightly weathered.

The ²⁹Si MAS-NMR and the deconvolution spectra of OPC was presented in Fig.5.4.9. It included spectrums for anhydrous OPC and 28-day hydrated pastes which were pre-cured at 25 and 85 °C.

Figure 5.4.9 ^{29}Si MAS-NMR spectra and the deconvolution spectra for anhydrous OPC of its 28-day pastes.

In Fig.5.4.9, the anhydrous cement exhibited a narrow, symmetrical signal centred over -71.5ppm and two shoulders, one at -70.2 ppm and the other at -73.4 ppm , denoting monomers (Q^0), which has been explained in chapter 4 (see Fig.4.4.9). After spectrum deconvolution (see Fig.5.4.9), the narrowest signal (-71.5 ppm) was attributed to belite (C_2S_{ss}) and the other two (-70.1 ppm and -73.4 ppm) to alite (C_3S_{ss}) components.

In the spectra of the hydrated cement after 28 days, it was observed a considerable decrease in the intensity of the signals associated with the anhydrous phases and the presence of new signals in the area between -79 and -85 ppm . This area is corresponded to the gel C-S-H (Bosque 2012). It shows

clearly three signals around -79 ppm, -82 ppm and -85 ppm in the spectrum. The data of the chemical shift with deconvolution along with the percentage of each peak was given in Table 5.4.7.

Table 5.4.7 Data for deconvoluted ^{29}Si MAS-NMR spectra for OPC.

Sample	OPC	Clinker			Hydrates		
		Q^0			Q^1	$Q^2(1Al)$	Q^2
Anhyd.	Pos.(ppm)	-70.2	-71.5	-73.4			
	Area (%)	25.52	20.81	53.67			
25°C	Pos.(ppm)	-70.2	-71.5	-73.4	-79.2	-82.2	-85.5
	Area (%)	10.87	20.21	20.75	22.16	14.41	11.60
85°C	Pos.(ppm)	-70.0	-71.5	-73.8	-79.2	-82.5	-85.5
	Area (%)	10.43	14.43	17.59	18.63	16.84	22.06

Most of the papers published on the ‘dreierketten’-type structure of C-S-H gel identify essentially two types of ^{29}Si MAS NMR signals: one at around -79 ppm associated with Q^1 (dimer or end of chain) units and the other -85 ppm attributed to $Q^2(0Al)$ (intra-chain) units (Richardson and Groves 1997, Andersen, Jakobsen et al. 2003). The resonance at around -82 ppm on spectra, was associated with the presence of $Q^2(0Al)$. Many authors (Richardson and Groves 1993, Schilling, Butler et al. 1994, Fernández-Jiménez, Puertas et al. 2003, Richardson 2014) agree that tetrahedrally coordinated aluminium can replace silicon in bridging positions (Q_B^2) in the C-S-H gel structure and shifts the ^{29}Si signal to -82 ppm. Anderson et al. (Andersen, Jakobsen et al. 2004) observed no aluminium replacements in paired or end-of-chain silicon tetrahedral by studying synthetic gels. These authors reported Al substitution for Si is not favoured in non-bridging sites. The presence of this signal in ^{29}Si spectrum correlated well with the resonance at around +65 ppm in ^{27}Al NMR spectra of the hydrated cement after 28 days (see Fig.5.4.8), which attributed to the presence of Al in tetrahedral bridging sites, characteristic of aluminium surrounded by two or three silicon.

With the deconvoluted data, the percentage of the various types of C-S-H gel units can be calculated with the area under each peak according to the equations listed in Table 5.4.9. The average chain length pre-curing at 85 °C (7.1) is higher than at 25°C (5.00), and the hydration degree of the paste has the same trends (57.6% compared to 48.2% at 25 °C). The data reveals that the average chain

length increases with increasing pre-curing temperature, in the other words; it means the gel C-S-H produced in the paste pre-cured at high temperature at 28 days is more polymerised. The ratio Al/Si (0.149 and 0.146 for 25 °C, 85 °C respectively) indicated that a little more Al was taken into the C-S-H gel when pre-cured at ambient temperature until 28 days.

Table 5.4.8 Ratios and equations used in the structural description of C-S-H and the calculating results for OPC pastes.

Ratios and equations	Richardson's equations for C-S-H (1994)		
	$n: \text{Al/Si} = 1/2 Q^2 (1\text{Al}) [Q^1 + Q^2 (0\text{Al}) + Q^2 (1\text{Al})]$ $* \text{MCL} = 2[Q^1 + Q^2 (0\text{Al}) + 3/2 Q^2 (1\text{Al})]/Q^1$ $* \alpha(\%) = (1 - Q^0) \times 100$		
	MCL	$\alpha(\%)$	Al / Si
Pastes pre-cured at 25 °C	5.0	48.2	0.149
Pastes pre-cured at 85 °C	7.1	57.6	0.146

n: the ratios Al and Si.

MCL: Mean chain length.

α : Hydration degree of the paste from deconvolution of MAS-NMR.

5.4.2.2 HYC

The ^{27}Al NMR-MAS spectra and its deconvolution for the anhydrous cement and the 28-day pastes pre-cured at the two temperatures are reproduced in Fig.5.4.10. The deconvolution data for 28-day pastes spectra was presented in Table 5.4.9.

For the anhydrous cement, the spectrum contained a wide asymmetrical signal centred on +59 ppm with a shoulder at around +80 ppm. The former was attributed to overlapping signals, which contained two signals (see Fig.5.4.10, the deconvolution spectra of anhydrous HYC), at around +60 and +41 ppm (see Table 5.4.9). These deconvoluted signals could be related to Al contents present in the raw hybrid cement; it contains clinker, BFS and FA composition. In the former section 4.4.3.2, it has been explained that the signals centred on +60 and +41 ppm were attributed to the Al_T present in the slag and fly ash (Puertas and Fernández-Jiménez 2003, García-Lodeiro, Fernández-Jiménez et al. 2013) and the shoulder at around + 80 ppm is associated to the Al_T in the clinker (Richardson and Groves 1997, Schneider, Cincotto et al. 2001, Andersen,

Jakobsen et al. 2003). The slightly intensity signals which related to Al_O could be come from little content of metastable calcium aluminate hydrate.

Figure 5.4.10 ^{27}Al MAS-NMR spectra for the anhydrous hybrid cement HYC and its 28-day pastes

When the cement was hydrated, the intensity of the +80 ppm (13.28% see Table 5.4.9) signal declined, meanwhile, a new peak at around +68 / +69 ppm appeared. The signal could be related to octahedral aluminium which was taken into the hydration product of clinker, C-(A)-S-H gel.

The signal at + 60 ppm presented in anhydrous HYC shifted to + 58 ppm, although it is definite that the signal is overlapping, the chemical shift also could indicate that reaction has been happened, which changed the octahedral Al surrounding. According to the literature (Puertas and Fernández-Jiménez 2003, Palomo, Alonso et al. 2004, García-Lodeiro, Fernández-Jiménez et al. 2013), this signal at +58 ppm was attributed to the presence of tetrahedral Al (Al_T),

possibly surrounded by three or four silicon atoms. The symmetry of this signal and the fact that it was narrower than the resonances in the starting materials suggested its possible association with the Al_T present in C-A-S-H- and (N,C)-A-S-H-like cementitious gels, as described in the literature (Richardson and Groves 1997, Garcia-Lodeiro, Palomo et al. 2011, García-Lodeiro, Fernández-Jiménez et al. 2013). However, this signal still should be considered as overlapping peak which contained Al_T presented in unreacted slag. The signal centred at + 41 ppm related to fly ash content still presents in hydrated pastes. This signal declined after 28 days in both two pastes (from 20.60% to 11.18 at 25 °C and 12.60 at 85 °C), the decline could be explained as pozzolanic reaction of fly ash.

Table 5.4.9 Deconvolution of ^{27}Al MAS-NMR spectra, showing signal position and area of HYC.

Sample	HYC	Al _T			Al _O			Al _T /Al _O
Anhyd.	Pos.(ppm)	79.95	60.15	41.17	10.10	0.96		
	Area (%)	13.28	58.90	20.60	1.41	5.27		
25 °C	Pos.(ppm)	70.07	58.25	42.35	13.18	9.15	5.60	
	Area (%)	5.84	43.61	7.48	14.02	19.31	9.74	
85 °C	Pos.(ppm)	68.99	58.70	43.36	/	10.09	5.00	
	Area (%)	6.71	32.34	12.60	/	36.06	13.54	

The new, very intense signals associated with octahedral aluminium (Al_O) appeared around +9 and + 13 ppm. For the sample pre-cured at 25 °C, two clearly separated signals were recorded. The signal at around +13 ppm was attributed to the Al_O in the ettringite, likewise detected with XRD. The signals at around +9.4 ppm may be associated with the presence of a small amount of octahedral Al (Al_O) in the form of calcium carboaluminate or calcium monosulfoaluminate, both compounds generate signals at around +10 / 9 ppm. As results, they are different to recognized by the deconvoluted signals (Faucon, Charpentier et al. 1998, Andersen, Jakobsen et al. 2003, Andersen, Jakobsen et al. 2006). The low intensity of the signal was more than likely attributable to its scant crystallinity. A small intensity peak at around +5 ppm (+4.98 ppm) should be related to TAH content.

When the cement was pre-cured at 85°C only 20h at beginning, the signal at +13 ppm was absent on spectrum and the signal at +9.4 shifted to +9.8 ppm (see Fig.5.4.10). That finding confirmed that no ettringite formed in the paste. The analysis of the spectra for the wide signal centred at + 9.8 ppm contained two signals, one is at + 10.09 ppm and the other is at + 5.00 ppm. The reference showed that U-Phase usually generated a signal at around + 10.3 ppm (Y. Shimada et al., 2004; M.J. Sánchez-Herrero et al., 2012). The peaks at + 10.09 could be associated with the U phase which detected in XRD patterns. At the same time, monocarboaluminate would generate a resonance at around + 10 / + 9 ppm, therefore, it could be overlap signal associated with U-Phase and AFm phase. The poorly defined signal at lower values (+5 ppm) is initially considered to be due to the presence of Al in gibbsite-like phases, which introduced before in OPC pastes. The assignation of ^{27}Al MAS-NMR deconvoluted peaks of HYC is listed in Table 5.4.10.

Table 5.4.10 ^{27}Al MAS-NMR deconvoluted peaks assignation of HYC.

Assignment	Chemical shift δ (ppm)		
	Anhydrous HYC	25 °C	85 °C
Clinker	79.95		
C-(A)-S-H		69.49	68.99
Slag + Fly ash	60.15		
C-A-S-H or (N,C)-A-S-H gel And unreacted slag + fly ash		58.79	58.70
Fly ash	40.17	44.05	43.36
$\text{C}_6\text{AS}_3\text{H}_{32}$ Ettringite		13.18	
Overlap of U-Phase and AFm			10.09
AFm		9.15	
TAH		5.60	5.00

The ^{29}Si MAS-NMR spectrum (see Fig.5.4.11) for the anhydrous cement exhibited a narrow, symmetrical signal centred over -71.5 ppm and two shoulders, one at -70.2 and the other at -73.8 ppm, denoting monomers (Q^0). The narrowest signal (-71.5 ppm) was attributed to belite ($\text{C}_2\text{S}_{\text{ss}}$) and the other two to alite ($\text{C}_3\text{S}_{\text{ss}}$) components. Alite and belite are the two main constituents of Portland clinker, and this signals coming from the 30% of clinker content in the raw materials. After spectrum deconvolution, a series of wide signals detected in addition to the aforementioned bands were assigned to the vitreous phase of the slag (see signals around -66, -74 and -77 ppm in Fig.5.4.11 and Table 5.4.11) (Puertas and Fernández-Jiménez 2003) The lowest intensity signal centred at around -107/-108 ppm, along with the one at -89 ppm, were associated with components in the fly ash.

Figure 5.4.11 ^{29}Si MAS-NMR spectra and the deconvolution spectra for the anhydrous hybrid cement HYC and its 28-day pastes.

The signals associated with the anhydrous phases declined significantly on the 28-day silicon spectra and new signals appeared in the -79 to -90 ppm range. The signals at around -79, -82 and -85 ppm were respectively generated by Q^1 (end-of-chain), Q^2 (1Al) and Q^2 (0Al) units, typical of C-(A)-S-H gels as mentioned before.

The signals positioned at more negative values, around -87.9, -92 and -97.8 ppm, might be associated with $Q^3(2Al)$, $Q^3(1Al)$ and $Q^3(0Al)$ units. The inference is

that very complex, highly polymerised structures, possibly a mix of C-(A)-S-H and C-A-S-H gels, were forming in the hybrid cement HYC.

Pre-curing at 85°C induce minor variations in the intensity of the signals comprising the 28-day gels. The ratio of less to more polymerised units ($Q^1+Q^2(\text{mAl})/Q^3(\text{mAl})$) was slightly higher in the material pre-cured at ambient temperature (2.9 compared to 2.5 at 85°C). Extrapolating to C-(A)-S-H/C-A-S-H gel formation, this finding denoted the generation of more C-(A)-S-H gel in the cement pre-cured at ambient temperature and more C-A-S-H in the material pre-cured at 85°C. The HYC exhibited a fairly low ($\approx 40\%$) CaO content and a higher ($\approx 12\%$) Al_2O_3 content than in OPC. Such circumstances would favour the uptake of Al in the linear silicon chains, which would in turn foster inter-chain cross-linking, giving rise to two-dimensional structures (Andersen, Jakobsen et al. 2003, Puertas and Fernández-Jiménez 2003). That result is consistent with the presence of a higher $\text{Al}_\text{T}/\text{Al}_\text{O}$ ratio in these cements than in ordinary Portland cement. The signal at +58 ppm in ^{27}Al NMR spectrum was an indication that in this case the Al_T was surrounded by several silicon atoms.

Table 5.4.11 Deconvolution of ^{29}Si MAS-NMR spectra for the anhydrous hybrid cement HYC and its 28-day pastes with their assignment.

Assignment	HYC anhydrous		HYC 28d 25 °C		HYC 28d 85 °C	
	Pos.(ppm)	A(%)	Pos.(ppm)	A(%)	Pos.(ppm)	A(%)
Q^0 Slag	-66.3	3.72	-67.0	5.01	-66.3	1.91
Q^0 C_3S	-69.8	8.67	-69.5	4.68	-69.1	2.70
Q^0 C_2S	-71.6	11.34	-71.6	10.59	-71.5	10.41
Q^0 C_3S	-73.0	8.45	-73.9	4.13	-73.4	6.67
Q^0 slag	-74.3	8.50	-75.5	2.20	-75.5	3.57
Q^1 slag	-77.6	26.16	-77.2	4.52	-77.7	4.47
Q^1 (0Al) C-S-H			-79.6	11.36	-79.9	9.17
Q^2 (1Al) C-(A)-S-H			-82.3	15.97	-82.0	6.07
Q^2 (0Al) C_3S			-85.6	13.29	-85.6	21.4
Q^3 (3Al) C-A/(A)-S-H			-87.9	3.47	-87.9	6.56
Q^4 (mAl) Fly ash	-89.0	8.03				
Q^3 (1Al) C-A/(A)-S-H			-92.2	5.20	-92.4	5.85
Q^3 (0Al) C-A/(A)-S-H			-97.8	5.04	-97.6	2.58
Q^4 Fly ash	-107.1	25.11	-107.1	14.54	-106.7	18.61

5.4.2.3 HYP

Fig.5.4.12 exhibits the ^{27}Al MAS-NMR spectra and the deconvolution and for the anhydrous hybrid cement HYP and its 28-day pastes. The deconvolution signal position is given by Table 5.4.12 with the area of each signal. The assignation of each peak is listed in Table 5.4.13.

Figure 5.4.12 ^{27}Al MAS-NMR spectra and the deconvolution spectra for the anhydrous hybrid cement HYP and its 28-day pastes.

The aluminium spectrum for the anhydrous cement contained a wide asymmetrical signal centred on +54 ppm with a shoulder at +80 ppm. The former signals centred at +54 ppm associated with tetrahedral aluminium in fly ash. The deconvolution spectra contain series of signals (+61.02 and 47.05 ppm respectively) related to fly ash content (Sánchez-Herrero 2017). The shoulder is primarily related to the Al_T in the surrounding C_3A , along with other clinker phases (Colombet and Grimmer 1994).

In general, when the cement was hydrated, the intensity of the +80 ppm signal declined and almost disappeared, which means the hydration of C_3A happen. The resonance at +54 ppm shifted to +58 ppm and new intense signals associated with octahedral aluminium (Al_O) appeared at around +13 / +9 ppm hydrated pastes samples. The phenomenon will be discussed combining with deconvolution information.

Table 5.4.12 Deconvolution of ^{27}Al MAS-NMR spectra, showing signal position and area of HYP.

Sample	HYP	Al_T			Al_O			Al_T/Al_O
Anhyd.	Pos.(ppm)	79.80	61.02	47.05	1.55	-5.27		
	Area (%)	20.64	31.05	40.02	4.11	4.18		11.1
25 °C	Pos.(ppm)	68.65	59.11	47.21	13.21	9.05	6.09	
	Area (%)	9.90	34.07	16.53	29.90	6.88	2.73	1.3
85 °C	Pos.(ppm)	67.39	59.00	45.52	10.22	2.50		
	Area (%)	4.73	27.90	15.02	38.79	13.57		0.9

Table 5.4.13 ^{27}Al MAS-NMR deconvoluted peaks assignation of HYP.

Assignment	Chemical shift δ (ppm)		
	Anhydrous HYP	25 °C	85 °C
Clinker	79.80		
Clinker		68.65	67.39
Fly ash	61.02	59.11	59.00
Fly ash	47.05	47.21	45.52
$C_6A\bar{S}_3H_{32}$ Ettringite		13.20	
Overlap of U-Phase and AFm			10.22
AFm		9.63	9.70
TAH		6.09	2.50
Fly ahs	1.55		

The 28-day spectrum pre-cured at 25 °C exhibits clearly signals located around +12.6 ppm and a shoulder around + 9 ppm. The deconvolution signal at +13.21 ppm was attributed to the Al_O in the ettringite whose exists has been confirmed by XRD. The signals at around +9.4 ppm may be associated with the presence of a small amount of octahedral Al (Al_O) in the form of calcium carboaluminate or calcium monosulfaluminate. In XRD pattern, carboaluminate has been detected. A small intensity peak at around +6 ppm (+6.09 ppm) should be related to TAH content as mentioned before. When the cement was pre-cured at 85°C, The analysis of the spectra for the wide signal centred at + 9.4 ppm contained two signals, the one at + 10.22 and the other on at + 2.5. As analysed in HYC, the signal at + 10.22 ppm could be related to U phase and AFm phases. The other at + 2.5 ppm should be associated the presence of Al_T in TAH.

Figure 5.4.13 ^{29}Si MAS-NMR spectra and the deconvolution spectra for the anhydrous hybrid cement HYP and its 28-day pastes.

^{29}Si MAS-NMR and the deconvolution spectra for the anhydrous hybrid cement HYP and its 28-day pastes can be followed by Fig.5.4.13. The ^{29}Si spectrum for the anhydrous cement gave a typical narrow peak at -71.6 ppm which was related to high contents of belite (C_2S_{ss}) in clinker. The lowest intensity but wide signal centred at around -107/-108 ppm was associated with components in the fly ash. After spectrum deconvolution, two wide signals detected (at -92 and -107 ppm) which assigned to the glassy component of fly ash in this hybrid cement (Fernández-Jiménez, Puertas et al. 2003). Although the spectra have been deconvoluted into two signals, these peaks are still overlapping resonance.

Table 5.4.14 gives the deconvolution details of hybrid cement HYP, including the peak position, the area of each peak and their assignation.

Table 5.4.14 Deconvolution of ^{29}Si MAS-NMR spectra for the anhydrous hybrid cement HYP and its 28-day pastes with their assignation.

Assignment	HYP anhydrous		HYP 28d 25 °C		HYP 28d 85 °C	
	Pos.(ppm)	A(%)	Pos.(ppm)	A(%)	Pos.(ppm)	A(%)
$\text{Q}^0 \text{C}_3\text{S}$			-69.80	1.56		
$\text{Q}^0 \text{C}_2\text{S}$	-71.70	23.62	-71.69	13.16	-71.72	17.70
$\text{Q}^0 \text{C}_3\text{S}$	-74.10	12.86	-73.34	1.71	-73.10	5.76
$\text{Q}^0 \text{C}_3\text{S}$			-75.91	1.98	-76.34	1.40
$\text{Q}^1(0\text{Al}) \text{C-S-H}$			-79.40	1.08	-79.77	13.36
$\text{Q}^2(1\text{Al}) \text{C-(A)-S-H}$			-81.55	6.78	-82.10	3.22
$\text{Q}^2(0\text{Al})$			-85.47	13.27	-85.21	11.31
$\text{Q}^4(4\text{Al})$ and/or $\text{Q}^3(3\text{Al})$	-89.49	10.31	-89.09	4.03	-88.08	4.75
$\text{Q}^4(3\text{Al})$ and /or $\text{Q}^3(1\text{Al})$			-93.07	3.20	-93.59	7.60
$\text{Q}^4(2\text{Al})$	Overlop signal		-95.51	5.29		
$\text{Q}^4(2\text{Al})$ and/or $\text{Q}^3(0\text{Al})$					-98.29	7.66
$\text{Q}^4(1\text{Al})$			-101.32	16.01	-103.0	13.30
$\text{Q}^4(0\text{Al})$	-107.17	53.21	-108.32	16.44	-107.72	13.02
Crystalline silica			-113.82	15.49	-115.00	10.89

In the 28 day ^{29}Si MAS NMR spectra for hydrated HYP, a new signal area appeared for pastes at both pre-cured temperature, which related to hydration product.

In the deconvolution signals at around -71.7 and -74 ppm which related to the tetrahedral Si monomers present in clinker components declined, confirming that the calcium silicates react. A new overlapping area from -80 to -90 ppm observed in both hydrated pastes (pre-cured at 25 °C and 85 °C) may be

associated with the hydration product gels. This area contains four deconvolution signals, at around -79.9, -82, -85 and -88 ppm. The former three signals could be associated with Q^1 , $Q^2(1Al)$, Q^2 units typical of a C-(A)-S-H gel. $Q^4(mAl)$ group units were detected, which could be related to (N,C) -A-S-H gel precipitated in HYP paste.

According to Table 5.4.14, concern should be taken of that the signals -89, -93, -98 ppm cannot be exactly related to Q^4 or Q^3 groups separately. They are overlapping signals. The signals related to the fly ash contents from -101 to -115 ppm, the sum of area of decreased after hydration, it could be explained the pozzolanic reaction of fly ash. However, the high intensity of the component associated with unreacted fly ash remained in hydrated paste samples, which reveals the existence of a large amount of unreacted ash.

5.4.2.4 FAN

Generally accepted worldwide, the denomination of N-A-S-H gel, used to be designated for the main reaction product formed in fly ash activation (Fernández-Jiménez and Palomo 2005). The alkali activation of fly ash is a process where the glassy constituents of the fly ash are transformed into compact cement (Fernández-Jiménez, de la Torre et al. 2006). The N-A-S-H gel formation model has been introduced in section 1.3.

In Fig.5.4.14, the changes in ^{27}Al MAS NMR between the original fly ash and activated fly ash are illustrated. The deconvolution values of ^{27}Al MAS-NMR spectra are listed in Table 5.4.15.

The ^{27}Al MAS NMR patterns for anhydrous fly ash contain two wide signals, one centered at +53 ppm (with two deconvoluted peaks, + 54.66 and + 52.90 ppm) associated with tetrahedral aluminium (Al_T) and a second small signal centered at +1.91 ppm, attributed to octahedral aluminum (Al_O), which is associated with the presence of original mullite component in the starting fly ash (Fernández-Jiménez, Palomo et al. 2006). During alkali activation, the tetrahedral aluminum signal is observed to shift from +53 to +58.6 ppm, indicating that the aluminium always remains tetrahedrally coordinated. The chemical shift for this resonance has been related to aluminium surrounded with four silica groups ($Al(-O-Si)_4$), which is characteristic of Al in zeolite precursors and N-A-S-H gels.

Figure 5.4.14 ^{27}Al MAS NMR and its deconvolution spectra (Right) for: anhydrous fly ash and activated 28 day pastes FAN with 8M NaOH.

Table 5.4.15 Deconvolution of ^{27}Al MAS-NMR spectra for the anhydrous fly ash and its 28-day pastes FAN.

Sample	FAN 28d	Al_T		Al_O
Fly ash.	Pos.(ppm)	54.66	42.90	1.91
	Area (%)	79.6	15.8	4.6
85 °C	Pos.(ppm)	58.6		-
	Area (%)	100		-

The ^{29}Si spectral of the anhydrous fly ash gives a very wide asymmetric signal formed by several components see Fig.5.4.15 (fly ash). The deconvolution spectrum gives us a series of wide signals, which are assigned to the components.

The peaks appearing about -84, -93.6, -98.6, -103.4 and -108 ppm are assigned to the glassy component of the fly ash (see Table 5.4.16). The peak at -88 ppm corresponds to the crystalline mullite presented in the ash, and the peaks at values of over -108 ppm are attributed to the presence of different crystalline phases of quartz.

Figure 5.4.15 ^{29}Si MAS NMR and its deconvolution spectra (Right) for: anhydrous fly ash and activated 28 day pastes FAN with 8M NaOH.

The spectra change substantially as the reaction progress (28 days) with five signals clearly visible at around -108 ppm, -104 ppm, -98 ppm, -93 ppm and -88 ppm (see Table 5.4.16). These resonances are respectively attributed to the presence of silicon tetrahedral surround by zero Q^4 (0Al), one Q^4 (1Al), two Q^4 (2Al), three Q^4 (3Al) and four Q^4 (4Al) aluminium tetrahedral, indicative of an N-A-S-H gel with a high silicon content (Smith, Kirkpatrick et al. 1983, Engelhardt and Michel 1987, Neuhoﬀ, Stebbins et al. 2003, Criado, Fernández-Jiménez et al. 2008). The signals appear at values higher than -108 ppm were

associated with $Q^4(0Al)$ units, i.e., silica polymorphs (Engelhardt and Michel 1987).

^{29}Si and ^{27}Al MAS NMR study illustrated that the N-A-S-H gel is three dimensional (3D), with the Si in a variety of environments and predominance of $Q^4(mAl)$ ($m=0, 1, 2, 3$ or 4) units (Fernández-Jiménez, Palomo et al. 2006) with certain Si/Al ratio (in this study, for paste FAN, $MNR_{Si/Al}=1.83$) according to Engelhardt equation. The Si^{4+} and Al^{3+} cations are tetrahedrally coordinated and joined by oxygen bonds. Aluminium is always surrounded with four silica groups, and Al atom should be uniformly distributed across the gel. The negative charge on the AlO_4^- group is neutralized by the presence of alkaline cations (Na^+).

Table 5.4.16 Deconvolution of ^{29}Si MAS-NMR spectra for the anhydrous fly ash and its 28-day pastes FAN; NMR Si/Al ratio by Engelhardt equation.

Assignment	Fly ash		FAN 28d 85 °C	
	Pos.(ppm)	A(%)	Pos.(ppm)	A(%)
$Q^2(mAl)$			-82.50	2.95
Fly ash $Q^4(4Al)$	-84.3	4.64	-85.76	6.62
Crystalline mullite Aluminosilicate gel $Q^4(4Al)$	-88.1	9.04	-88.63	14.36
Fly ash Aluminosilicate gel $Q^4(3Al)$	-93.6	17.35	-93.34	27.47
Fly ash Aluminosilicate gel $Q^4(2Al)$	-98.3	19.79	-98.79	20.55
Fly ash Aluminosilicate gel $Q^4(1Al)$	-103.2	21.47	-103.9	16.31
Fly ash $Q^4(mAl)$ Aluminosilicate gel $Q^4(0Al)$	-108.5	23.39	-108.4	4.50
Silica polymorphs			-111.4	5.49
Silica polymorphs	-116.0	4.34	-114.7	1.79

Engelhardt equation for aluminosilicate materials (1987) When $n = 4$ and $0 \leq m \leq 4$

$$\left(Si/Al = \frac{\sum_{m=0}^4 I_{Si(mAl)}}{\sum_{m=0}^4 \frac{m}{4} I_{Si(mAl)}} \right)$$

$I_{Si(mAl)}$ is the intensity of the Si-associated component surrounded by mAl and $(4-m)$ Si units.

5.4.3 Microscopy study and discussion

5.4.3.1 OPC

Fig.5.4.16-17 exhibited the results of 28-day pastes samples under scanning electron microscopic (SEM/EDX) techniques. The samples were analysed to confirm the hydration products of OPC.

In the micrographs OPC (Fig.5.4.16 and Fig.5.4.17), we observed a cementitious matrix consisting mainly of Ca and Si with little Al, which confirmed the formation of gels C-S-H/C-(A)-S-H. The presence of portlandite crystalline phase (in blue rectangle) is detected as the important hydration product along with the gel.

Figure 5.4.16 SEM and EDX analysis of 28-day OPC pre-cured at 25 °C.

Figure 5.4.17 SEM and EDX analysis of 28-day OPC pre-cured at 85 °C

In regard to the effect of curing temperature, the difference is that the presence of long ettringite needles pre-cured at 25 °C was observed together with the gel. However, with the initial pre-curing at 85 °C (first 20 hours), ettringite was not observed by SEM, confirming previous results obtained by XRD and NMR.

5.4.3.2 HYC

The 28-day samples studied under NMR were analysed with scanning electron microscopic (SEM/EDX) techniques to confirm the formation of one or several gels in the hybrid cement. The results are shown in Fig.5.4.18-5.4.19. These micrographs showed that the materials pre-cured at both 25 and 85°C had a fairly compact microstructure.

A number of un-reacted spherical ash particles embedded in the 28-day cementitious matrix were observed. The clinker and slag particles were more difficult to distinguish morphologically. As the microanalyses show (Fig.5.4.18, points 1, 2, 3 and 4), in addition to Ca and Si, the gel formed contained Al and some Na. The variations in gel composition were attributed to the fact that they were forming alongside a clinker, slag or ash particle, which would confirm the formation of a C-(A)-S-H, C-A-S-H and (N,C)-A-S-H-like mix of gels. Another finding worthy of note was the presence of a small amount of Na (see

microanalysis), sourced from the solid alkaline activator used to manufacture the cement. The sodium was fixed in the cementitious gel to balance the charge deficit generated when a silicon tetrahedron was replaced by an aluminium tetrahedron.

As far as the effect of temperature is concerned, the XRD analyses detected no ettringite at any age (3, 28 or 90 days) in the pastes pre-cured at 85 °C for 20 h. This also can be observed in SEM, in similar pore structure, Portladite was observed instead of ettringite in the pasted pre-cured at 85°C. Nonetheless, SEM revealed the presence of sulfates throughout the matrix, in all likelihood the result of the adsorption of the sulfates present in the aqueous phase onto the gel surface. Many of the references in the literature to the uptake of sulfate ions on/into the C-S-H gel surface/structure (Fu, Xie et al. 1994, Thomas, Rothstein et al. 2003) report that this development is favoured by the presence of alkalis and high curing temperatures. Nonetheless, the impact of the sulfate ions absorbed onto the gel structure has yet to be determined. In contrast, the risk posed by the release of those ions at mature cement ages and concomitant delayed ettringite formation is better understood (Taylor, Famy et al. 2001, Collepardi 2003).

The variations revealed by NMR and SEM in the composition and structure of the gels also merit comment. When initial curing took place at 85°C, more C-A-S-H than C-(A)-S-H gel formed. High curing temperature and the presence of alkalis are known to hasten calcium silicate hydration in clinker and C-S-H gel nucleation, although these two parameters also lower calcium hydroxide solubility (Fu, Xie et al. 1994, Collepardi 2003) and consequently the amount of this compound available for ettringite formation. At the same time, higher temperature and alkalis raise the solubility of the Si and Al in SCMs (Escalante-Garcia and Sharp 2000) (ash and slag in this case). Therefore, with the rise in pre-curing temperature, the aqueous phase would be expected to contain larger amounts of Si and Al ions and smaller amounts of Ca ions. That would favour the speedier precipitation of C-A-S-H than C-(A)-S-H gels. C-A-S-H gel formation around un-reacted particles early into the reaction would explain the high 3-day strength observed in the cement pre-cured at 85 °C. This possibly less permeable gel would hamper the diffusion and subsequent hydration of anhydrous particles, however, explaining the lesser rise in mechanical strength observed.

Point	O	Ca	Al	Si	S	Na	Fe	K	
1	56.0	28.2	2.4	10.1	0.6	1.1	0.6	0.01	C-(A)-S-H
2	58.9	16.2	3.8	14.9	1.7	2.6	0.6	0.24	C-A-S-H
3	58.4	19.3	8.7	11.6	0.6	0.8	0.0	0.30	C-A-S-H
4	50.0	49.7	0.0	0.0	0.0	0.0	0.3	0.0	Ca(OH) ₂

Figure 5.4.18. SEM and EDX analysis of 28-day HYC pre-cured at 25 °C.

Point	O	Ca	Al	Si	S	Na	Fe	K	
1	61.4	3.9	11.4	15.4	0.3	1.4	1.9	0.7	(N,C)-A-S-H
2	56.2	17.9	7.0	8.7	1.7	5.7	0.9	0.6	C-A-S-H
3	57.5	16.5	8.2	11.7	0.8	1.9	0.2	0.2	C-A-S-H
4	50.6	47.7	0.0	0.8	0.0	0.0	0.8	0.0	Ca(OH) ₂

Figure 5.4.19. SEM and EDX analysis of 28-day HYC pre-cured at 85 °C.

That would favour the speedier precipitation of C-A-S-H than C-(A)-S-H gels. C-A-S-H gel formation around un-reacted particles early into the reaction would explain the high 3-day strength observed in the cement pre-cured at 85 °C. This possibly less permeable gel would hamper the diffusion and subsequent hydration of anhydrous particles, however, explaining the lesser rise in mechanical strength observed.

5.4.3.3 HYP

Fig.5.4.20-5.4.21 exhibited SEM/EDX analysis for the 28-day samples that studied under NMR. These techniques used to confirm the formation of one or several gels in the hybrid cement HYP.

As the microanalyses showing (Fig.5.4.20 and Fig.5.4.21 points 1, 2, 3 and 4), in addition to Ca and Si. The gel formed contained Al and some Na. The variations in gel composition were attributed to the fact that they were forming alongside a clinker or ash particle, which would confirm the formation of a C-(A)-S-H, C-A-S-H and (N,C)-A-S-H-like mix of gels.

Together with the other technique, the obvious fact is that ettringite was not formation in all the paste pre-cured at 85°C at any tested age. Although ettringite was detected by XRD analysis in the pastes pre-cured at 25°C for 20 h at 28 day; it was not clearly observed at the micrographs. Sulphates were obtained throughout the matrix the same as cement HYC, which could be attributed to the adsorption of sulphates present in the aqueous phase onto the gel surface. This adsorption happened faster at high temperature (Fu, Xie et al. 1994). Slower release of sulphate from an internal sulphate source may be critical for delayed ettringite formation.

The SEM image for paste pre-cured at 85 °C looked compact and foil-like. The gel formed contained more Si and Al content and small amount Ca. Combined with the analysis of NMR, more C-A-S-H gel formation at 85 °C. With high pre-curing temperature, pozzolanic reaction was also accelerated in the first 20 hours, which could contribute to gel precipitation around the particles.

Point	O	Ca	Al	Si	S	Na	Fe	K	
1	60.2	9.5	10.4	13.0	1.7	2.2	0.7	1.0	C-(A)-S-H
2	57.3	26.6	2.8	9.0	2.2	0.8	2.3	0.4	C-A-S-H
3	59.2	16.1	8.3	9.2	2.5	1.2	1.3	0.5	(N,C)-A-S-H
4	59.9	11.7	8.8	12.6	1.7	1.5	0.9	0.9	C-A-S-H

Figure 5.4.20 SEM and EDX analysis of 28-day HYP pre-cured at 25 °C.

Point	O	Ca	Al	Si	S	Na	Fe	K	
1	57.1	25.6	3.1	10.1	1.5	1.1	0.5	0.3	C-(A)-S-H
2	59.8	14.9	9.0	8.6	2.8	0.9	2.1	0.9	C-A-S-H
3	60.7	8.0	11.4	12.4	1.4	1.0	2.7	1.6	(N,C)-A-S-H
4	57.6	15.5	6.6	10.4	1.5	1.8	1.6	1.5	C-A-S-H

Figure 5.4.21 SEM and EDX analysis of 28-day HYP pre-cured at 85 °C.

5.4.3.4 FAN

From the chemical standpoint alkali activation of fly ash is a process that is different to Portland cement hydration. As introduced before, the main reaction products in the alkali activation of fly ash is an alkaline aluminosilicate gel, N-A-S-H gel. This product is structured around tetrahedrally co-ordinated silicon

and aluminium, forming a polymer chain in which the Al^{3+} ions replace the Si^{4+} ions. The resulting net anionic charge is compensated by the capture of monovalent alkaline cations. NMR results (in the section 5.4.2) confirmed that aluminium is always surrounded with four silica group and Al atom should be uniformly distributed across the gel.

On the other hand, the process of AAFA is very similar to the chemistry involved in the synthesis of large groups of zeolites (Querol, Moreno et al. 2002, Palomo, Alonso et al. 2004). Zeolites are group of hydrated framework aluminosilicates that incorporate molecular H_2O in structural pores. According to the authors, the alkaline aluminosilicate gel (N-A-S-H) is described as a precursor of certain crystalline zeolite species. Meanwhile, different types of zeolites are normally formed as secondary reaction products in AAFA system.

In this work, sodium hydroxide which is the most common activator was used to react with fly ash. In XRD, signals were detected corresponding to zeolite structure such as hydroxysodalite and herschelite. In this part, SEM and EDX are used to study the morphology of this paste.

Figure 5.4.22 SEM and EDX analysis of 28-day FAN paste.

Fig.5.4.22 exhibited the SEM micrographs and EDX analysis of the matrix after alkaline activation of fly ash (FAN paste). A massive and uniform gel was observed. This gel formed along with ash particle. Point 1 and point 2 give the EDX information related to N-A-S-H gel with Si/Al ratio 1.82 and 1.43 respectively. It is clearly to see that inside and outside the fly ash particles, gel has been precipitated under the function of alkalis attack.

Figure 5.4.23 SEM image of herschelite and EDX analysis.

Figure 5.4.24 Details of herschelite SEM image.

Another interesting SEM finding was the presence of rosette-like aggregates (see Figure 5.4.23). It resembles synthetic zeolite morphology. Herschelite appears to have a framework isostructural with that of chabazite. It is listed as a separate species based upon the differences in chemical composition and physical properties. From the Figure 5.4.24, it is interesting to obtain that the

structure of herschelite is various with different number of “petals”, this is due to the crystalline growth of herschelite is crosses. The single “petal” crystalline could be hydroxysodalite.

5.5 Discussion

The selected pre-curing condition at higher temperature (at 85 °C) was only at the beginning twenty hours. The mechanical strength of pastes and mortar give the same trends when comparing two hybrid cements and reference OPC. In the early ages (three days), higher pre-curing temperature contributed better mechanical strength dramatically. The reason is when pre-cured at higher temperature; the hydration of main clinker phase's rate of materials is accelerated by hours, which was confirmed by the analysis of reaction kinetics. Before 20 hours (see Fig.5.3.1-5.3.3) the main reaction happened with stable final cumulative heat release. In mature pastes (after 28 days), the specimens pre-cured at ambient temperature (25 °C) performed better mechanical behaviour than that pre-cured at higher temperature (85 °C).

For OPC, the reason for strength observation was explained by some authors ([Escalante-Garcia and Sharp 2000](#), [Elkhadiri, Palacios et al. 2009](#)): A high initial rate of hydration induces the non-uniform distribution of the hydration product across the microstructure, with dense clusters forming around the hydration grains and retarding subsequent hydration. The resulting increase in porosity has an adverse effect on long-term strength.

Alkali-activated fly ash (FAN) gives the results that, after 20 hours at 85 °C, it gained good mechanical behaviour due the participation of main product: an alkaline aluminosilicate gel (N-A-S-H gel). The curing temperature plays very important role in alkali activated fly ash-cement. As introduced before, the increase of the curing temperature from 45 °C to 65 °C increases by five times the velocity of mechanical strength development; and the increase of curing temperature from 65 °C to 85 °C increases by ten times this velocity ([Palomo, Grutzeck et al. 1999](#)). In our study, with ambient temperature (25 °C) pre-curing, the reaction of alkali-activated binders did not happen (no data recorded in calorimetric curves) and FAN pastes did not harden. It is due to the raw fly ash materials dissolution calls for high temperature and alkalinity.

How pre-curing temperature effect hybrid cements is not clearly studied. According to the composition of raw materials, and the experiments finding described in this chapter, the reaction process could be discussed as following.

Rietveld XRD results showed that although HYC and HYP contained low clinker content, C_3S , C_2S , C_3A and C_4AF also presented as phases in the raw materials. When hybrid cements hydrated with water, the main hydration reaction in phases of Portland cement (see Table 1.1.2) happened in the process as well. The main product is C-S-H gel and the second products are such as portlandite, ettringite. However, the additions of supplementary cementitious materials (BFS and FA) and solid activator in raw materials of hybrid cements make hydration process behave in a different way and additional reactions take place.

In general, FA is usually used as man-made pozzolans admixture in modern concrete. They can react with $Ca(OH)_2$ and water in long time, which is called pozzolanic reaction. The reaction product normally is C-S-H gel with consumption of calcium hydroxide (Dodson 1990). It could be described as:

In the process, $Ca(OH)_2$ (portlandite) hydrolyses in the system first and improved the solution pH value very quickly (Caijun Shi, Robert L. Day, 2000) and released Ca^{2+} and OH^- into solution:

Under the attack of OH^- in such a high pH value solution, silicate and/or aluminosilicate networks in the supplementary materials depolymerized and dissolved as monosilicate and aluminate species into the solution which can be introduced as follows in Eq.(3) and Eq.(4):

When Ca^{2+} ions contacted these dissolved monosilicate, C-S-H gel formed (Caijun Shi, Robert L. Day, 2000):

In this work, two hybrid cements contain solid activator when they were manufactured. Both solid activators used in hybrid cement manufacture are mixture of salts with dominant component of Na_2SO_4 . As introduced in chapter one, mildly alkaline activators are usually used to activate hybrid cement system because the reaction product, $\text{Ca}(\text{OH})_2$, of on-going Portland cement clinker, can raise the pH in the medium by their synergetic reaction. The process can be described as set out below:

The pH in the medium could be increased by the presence of component of Na_2SO_4 in order to accelerate the reaction of SCMs to dissolve into the solution. In the other hand, the presence of sulphates is known to favour ettringite formation in standard OPC, meanwhile the SO_4^{2+} anion may alter C-S-H gel characteristics though the way of being adsorbed but not chemically bound as SO_4^{2+} , requiring Ca^{2+} to balance the negative charge (Agulera J, 2003, Nicoleau. L et al. 2014). In a recent research on alkaline hydration of different synthesized phases (C_3S , C_2S , C_3A) by Sánchez-Herrero et al., (2012, 2016), the presence of Na_2SO_4 can raise the mechanical strength of pastes, which in this work, our results of hybrid cements are in good agreement.

When the hybrid cement was pre-cured at 25 °C the reaction of hybrid cements start with hydration of clinker phases to generate C-S-H and portlandite (pH ~12.5). The gel C-S-H probably takes aluminium into its composition in bridge position, yielding C-(A)-S-H then to C-A-S-H gels as the aluminium content rises. $\text{Ca}(\text{OH})_2$ then reacts with the inorganic salts of activator (mainly Na_2SO_4) to generate the respective insoluble calcium salt and $\text{Na}^+(\text{OH})^-$ (pH > 13) raising medium alkalinity as Eq. 6. In addition, the heat released during initial clinker phase hydration favours and expedites the dissolution of SCMs at this higher pH, favoured the formation of (N,C)-A-S-H gel, and a mixture of gels are obtained.

The mature age samples (28 and 90 days) performed acceptable compressive strength for both HYC and HYP cements. It was due to the continuous hydration of clinker phases (C_3S mainly) and the reaction of SCMs. For hybrid cement HYC, BFS content should be activated in high pH environment to form C-A-S-H gel. The hydration of HYC is complex by the co-reactions: hydration of clinker phases, pozzolanic reactions and alkali-activating reactions. The finding of MAS-NMR and SEM / EDX exhibited that the main hydration product is a mix of cementitious gels C-(A)-S-H + C-A-S-H, which was contributed to the co-reactions (see Figure 5.5.1 and 5.5.2).

Figure 5.5.1 The relationship of different type of gels.

Figure 5.5.2 . Plot of SEM-EDX gel data points as a function of CaO, SiO₂ and Al₂O₃ content for 90 days pastes of two hybrid cements pre-cured at 25 and 85 °C.

Raising the pre-curing temperature from 25 to 85 °C accelerated the initial reaction in hybrid cements studied, which exhibited 3-days compressive strength values of around 30 MPa for both HYC and HYP. Nonetheless, the subsequent development of mechanical strength was slower than when the cements were pre-cured at ambient temperature.

When the pre-cure temperature is 85 °C, all reactions are faster, especially the solubility of SCMs (fly ash and slag). The calorimetric and XRD findings indicated that raising the curing temperature from 25 to 85 °C in the first 20 h of the reaction expedites initial hydration in hybrid cements. The high initial alkalinity produced by the reaction between the activator with portlandite together with a higher initial temperature (85 °C), favours the rapid dissolution of the SCMs (Escalante-Garcia, and Sharp, 2000) (ash and slag), higher temperature and alkalis raise the solubility of the Si and Al from SCMs. High curing temperature and the presence of alkalis are known to hasten calcium silicate hydration in clinker and C-S-H gel nucleation, although these two

parameters also lower calcium hydroxide solubility (Thomas, D. Rothstein, et al., 2013). Therefore, with the rise in pre-curing temperature, initially the aqueous phase would be expected to contain larger amounts of Si and Al ions and smaller amounts of Ca ions than when the binder is pre-curing is at 25 °C.

The presence in the medium of elevated Ca and Si contents from OPC together with a greater initial contribution of Si and Al from the SCMs favours the precipitation of different gels. The gels type C-A-S-H near the particles of OPC and slag and gels type (N, C) -A-S-H and even N-A-S-H near the ash particles, forming a clusters. It to say curing at 85 °C a greater initial degree of reaction is obtained. That would explain the high 3-day mechanical strength values. At longer reaction times, however, the beneficial effect of a higher pre-curing temperature was attenuated, whereas in the mortars pre-cured at ambient temperature mechanical strength continued to rise in all cement. That may be because the reaction products that formed rapidly in the cements pre-cured at 85 °C built a barrier around the unreacted particles, delaying their hydration. This possibly less permeable gel would hamper the diffusion and subsequent hydration of anhydrous particles (both OPC and SCMs) however, explaining the lesser risen mechanical strength observed. Figure 5.5.2 exhibited the plot of SEM-EDX gel data points of 90-day pastes of two hybrids cement. The pastes pre-cured at 85 °C presented a cluster of gels with more CaO content, which could be explained by the lower interaction previously indicate.

Another interesting finding is when the pastes prepared at high temperature (at 85 °C), ettringite were absent. Another new mineralogical phase detected was U-phase in HYC and HYP pastes. For its formation, requires both SO_4^{2+} and Na^+ ions, but also high pH in the medium (Li, Le Bescop et al. 1996). The SO_4^{2+} and Na^+ ions were come from solid activator by the reaction Eq. 6. Li et al., (1996, 1997) overserved that once U-phase forms, a decline in alkalinity induces its conversion first to calcium nomosulfoaluminate and then to ettringate. The author summarized their observations in the following expression:

The presence of this phase indirectly provides information on medium pH and confirming the reaction of the Eq.5.5.6.

5.6 Concluding remarks

This report on an industrial hybrid cements with a low clinker content manufactured with an alkaline activator shows that the production of cements with a very low clinker factor and high mechanical strength is feasible. Industrial hybrid cements (HYC and HYP) owes its good mechanical strength to the main

hydration product, a mix of cementitious gels (N, C)-A-S-H+C-(A)-S-H + C-A-S-H. These gels take up a larger percentage of aluminium and are more intensely polymerised than traditional C-S-H gel.

The main reaction product of alkali-activated fly ash is an alkaline silicoaluminate gel (N-A-S-H gel), which was reported by some works (Criado, Palomo et al. 2005, Fernández-Jiménez and Palomo 2005, Kovalchuk, Fernández-Jiménez et al. 2007). The product of this material was strongly affected by the type of activator and the curing condition. Unlike other cementitious binders, the mechanical strength is strongly influenced by the curing temperature; at 25 °C the material does not harden in time technologically viable.

In hybrid cements HYC and HYP, a high pre-curing temperature expedites hydration reactions in much the same way as in OPC and alkaline cements. Raising the temperature from 25 to 85 °C accelerated the initial reaction in the cement studied, which exhibited 3-day compressive strength values of up to 30 MPa. Nonetheless, the subsequent development of mechanical strength was slower than when the cement was pre-cured at ambient temperature. Initial curing at 85°C for 20 h induced the formation of more polymerised gels (lower ratio) and inhibited ettringite formation (or favoured its swift decomposition), at least during the first 90 days, the maximum age of the materials analysed here. The possibility of delayed ettringite formation (DEF) at later ages in these thermally pre-cured hybrid cements cannot therefore be ruled out.

Therefore, although curing at 85°C accelerates the initial development of resistances in Portland cement and hybrid cements (HYC and HYP), given its lower evolution over time and the risk posed by the possible formation of EDF, it was considered that curing at room temperature as the most appropriate option for the next work. However, in the case of fly ash binder (without OPC), the pre-curing selected was 20 h at 85 °C.

6 *High temperature mechanical and physicochemical behaviours*

6.1 Introduction

Cement-based materials are non-flammable and offer significant safety advantages over wood and plastic and help protect steel rebar in structural concrete. However, fire events and high temperature exposure can cause significant damage to PC (Portland cement) based materials.

Subjecting concrete to high temperature (e.g., due to accidental fire, chimney etc.) leads to severe deterioration. It undergoes a number of transformations and reactions, thereby causing progressive breakdown of cement gel structure and consequent loss in its load-bearing capacity, reduced durability, increased tendency of drying shrinkage, structure cracking and associated aggregate colour changes (Diamond 1972, Khoury 1992, Handoo, Agarwal et al. 2002).

As multiphase materials, complex physicochemical transformations take places in cement pastes (Portland Cement) when they are exposed to high temperature (Piasta 1984, Brough, Dobson et al. 1994, Bentz 1999). The property changes of pastes with temperature could be caused by chemical transformation, micro-cracking and microstructure changes (Zhang 2013), which is a key factor for concrete fire-behaviour.

In this chapter, the main goal is to study mechanical properties of three types of cement paste: Portland cement (CEM I 42.5 (OPC) as reference), two pre-industrial hybrid cements (HYC and HYP) and a alkali-fly ash cement FAN (fly ash-activated with NaOH solution). The study was designed to study, also the physicochemical behaviour of different cement pastes with temperature.

According to the previous results obtained in chapter 5, the samples selected are OPC, two hybrid cements, HYC and HYP hydrated with water and pre-cured at 25 °C after 28 days. FAN pastes are prepared with 8 M NaOH as activator and pre-cured at 85 °C for 20 hours, also after 28 days. The conditions of preparing four binder materials and compressive strength were listed in Table 6.1.1.

Table 6.1.1 The pastes preparation information

Materials	Liquid /Activador	Pre-curing temperature	Liquid/Solid ratio	Compressive strength at 28 days (MPa) (10 ×10 ×60 mm)
OPC	water	25 °C	0.3	73
HYC	water	25 °C	0.3	57
HYP	water	25 °C	0.3	48
FAN	8M NaOH	85 °C	0.3	27

Two types of mechanical tests were conducted on pastes samples made of each of these three cementitious systems: i) high-temperature in-situ mechanical tests, including bending and compressive strength, fracture toughness and modulus of elasticity (see section 3.2.2 for detailed information); ii) post-thermal treatment tests, which evaluate residual strength after two hours of exposure to temperatures ranging from 400 °C to 1000 °C, which including two cooling processes, in water and air (see section 3.2.1.3 for detail information).

To study mineralogical and microstructural variations of hydrated binder materials, different techniques were used as well: differential thermo-gravimetric (DTA)/TG, X-ray diffraction, MAS NMR studies, SEM / EDX and Hg porosimetry. All the tests were conducted on the sample after thermal treatment.

Comprehensive analysis on the binders should provide new ideas about the relationship between the elemental composition of materials and high-temperature mechanical performance.

6.2 Mechanical behaviour of materials tested in-situ evaluated temperature

As previously commented in chapter 2, one of main objective of this work is to investigate high temperature durability of different types of cements. In this part, the study is to determine the mechanical behaviour of binders at which was tested in-situ evaluated temperatures.

The tested condition and specimen's information were introduced in section 3.2. It is worth noting that the specimens of 1) $4 \times 4 \times 14$ mm; 2) $4 \times 14 \times 50$ mm; were prepare from a single block ($100 \times 100 \times 60$ mm) of pastes. The reason is to ensure sample uniformity.

Compressive test was conducted on samples with size of $4 \times 4 \times 14$ mm from ambient temperature (25 °C) to 1000 °C. Fracture behaviour was studied using TPB (three point bending) tests performed on specimens with size of $4 \times 14 \times 50$ mm, which included flexural strength test, fracture toughness test and fracture surface SEM study. Specific work has been explained in section 3.3.2. An original and unprecedented procedure was devised to notch the samples for the fracture toughness tests, in which notch tip of around 10 µm were attained, i.e., more than one order of magnitude lower than normally achieved with diamond wire saws.

In all cases, the specimens were subjected to a preload during heating to fasten them securely to the testing device. In compressive tests the preload is around 5 N, in flexion and fracture toughness tests the preload is around 2N. At very high temperature, this caused, in some cases, pronounced deformation before failure, which occurred at low loads, or spontaneous specimen failure during heating due to the deterioration of its properties at high temperature. These behaviours determined the maximum characterization temperature for each material.

All the tests were subjected to temperature of up to 200 °C at an incremental ratio of 4 °C per minute from room temperature. After 200 °C, the ratio was improved to 20 °C per minute until the target temperature. Once the temperature was attained, the specimens were stabilized for twenty minutes before proceeding to run the test. After that, the furnace was switched off and the specimens were allowed to cool naturally to room temperature. The low initial incremental ratio (4 °C/min) was selected experimentally to avoid thermal damage to specimens which might cause premature failure (Fernández-Jiménez, Palomo et al. 2008, Fernández-Jiménez, Pastor et al. 2010). Since in this range of temperature a lot of chemical reactions are happening in the material, and a fast heating can introduce significant residual stresses that in many cases can break spontaneously the specimen.

6.2.1 In situ compressive test

Compressive strength is one most common property of cement-based materials used for structural design. The present study specifically examines the pastes compression behaviour under loading while the specimen is heated; here we called in-situ compressive strength. The stress and strain values were calculated from equation 3.1 and 3.2, which were explained in former section.

Fig.6.2.1 to Fig.6.2.4 show the full test of stress-strain curves of selected pastes of materials (OPC, HYC, HYP and FAN) for in situ compression test at evaluated temperature. In the curves, the elastic zone is delimited by yield stress. A line is constructed parallel to the initial portion of the stress-strain curve but offset by 0.2% from the origin, which was drawn when the materials behave plastic behaviour.

Strength values in compression test was calculated and listed in Table 6.2.1 to 6.2.4. In the Table σ_u and ϵ_u are the ultimate strength and its corresponding ultimate strain; σ_y and ϵ_y are the yield strength at 0.2% offset and its corresponding yield strain respectively. These values are obtained by the

intersection point between the drawing lines and stress-strain curves. Each value comes from the value of the mean of three tests and standard error (SE) was used in error analysis.

Figure 6.2.1 In-situ compression test stress-strain curves at different temperatures of OPC. (Figure a) is full stress-strain curve at all temperature, Figure b) is replot of Figure a) at 25, 400 and 600 °C; Figure c) is full stress-strain curve at 800 and 1000 °C; Figure d) is enlargement of local area of Figure c)).

Table 6.2.1 Values of compressive strength and strain of OPC in in situ compression test at elevated temperature (mean value $\pm$ standard error).

OPC	Target temperature (°C)				
	25	400	600	800	1000
σ_u (MPa)	110 $\pm$ 10	81 $\pm$ 4	43 $\pm$ 9	6.8 $\pm$ 0.6	/
ε_u (%)	1.51 $\pm$ 0.09	2.68 $\pm$ 0.15	2.09 $\pm$ 0.23	10.03 $\pm$ 1.64	/
σ_v (MPa)	/	76 $\pm$ 8	41 $\pm$ 8	1.4 $\pm$ 0.1	1.00 $\pm$ 0.05
ε_v (%)	/	2.32 $\pm$ 0.25	1.87 $\pm$ 0.11	0.37 $\pm$ 0.02	0.29 $\pm$ 0.02

Figure 6.2.2 In-situ compression test stress-strain curves at different temperatures of HYC. (Figure a) is full stress-strain curve at all temperature, Figure b) is replot of Figure a) at 25, 400 and 600 °C; Figure c) is full stress-strain curve at 800 and 1000 °C; Figure d) is enlargement of local area of Figure c)).

Table 6.2.2 Values of compressive strength and strain of OPC in in-situ compression test at elevated temperature (mean value $\pm$ standard error).

HYC	Target temperature (°C)				
	25	400	600	800	1000
σ_u (MPa)	86 ± 5	84 ± 6	43 ± 2	16.4 ± 1.3	5.7 ± 0.6
ε_u (%)	1.53 ± 0.02	2.71 ± 0.38	3.82 ± 0.29	5.91 ± 0.89	4.13 ± 1.23
σ_v (MPa)	/	76 ± 2	32 ± 1	5.8 ± 1.1	2.3 ± 0.1
ε_v (%)	/	2.00 ± 0.06	1.88 ± 0.18	0.88 ± 0.25	0.36 ± 0.02

Figure 6.2.3 In-situ compression test stress-strain curves at different temperatures of HYP. (Figure a) is full stress-strain curve at all temperature, Figure b) is replot of Figure a) at 25, 400 and 600 °C; Figure c) is full stress-strain curve at 800 and 1000 °C; Figure d) is enlargement of local area of Figure c)).

Table 6.2.3 Values of compressive strength and strain of OPC in in-situ compression test at elevated temperature (mean value $\pm$ standard error).

HYP	Target temperature (°C)				
	25	400	600	800	1000
σ_u (MPa)	85 ± 4	69 ± 1	27 ± 3	20.5 ± 1.5	12.5 ± 0.8
ε_u (%)	1.42 ± 0.07	2.57 ± 0.08	3.25 ± 0.40	6.02 ± 1.37	2.51 ± 0.40
σ_y (MPa)	/	61 ± 1	23 ± 3	11.3 ± 0.9	5.2 ± 0.8
ε_y (%)	/	1.91 ± 0.04	2.25 ± 0.24	1.76 ± 0.41	0.48 ± 0.09

Figure 6.2.4 In-situ compression test stress-strain curves at different temperatures of OPC. (Figure a) is full stress-strain curve at all temperature, Figure b) is replot of Figure a) at 25, 400 and 600 °C; Figure c) is full stress-strain curve at 800 and 1000 °C; Figure d) is enlargement of local area of Figure c)).

Table 6.2.4 Values of compressive strength and strain of OPC in in-situ compression test at elevated temperature (mean value $\pm$ standard error).

FAN	Target temperature (°C)				
	25	400	600	800	1000
σ_u (MPa)	20 ± 2	37 ± 5	82 ± 7	/	/
ϵ_u (%)	1.42 ± 0.07	2.57 ± 0.08	10.92 ± 0.69	/	/
σ_v (MPa)	/	/	79 ± 10	1.53 ± 0.09	0.53 ± 0.08
ϵ_v (%)	/	/	7.31 ± 0.52	0.33 ± 0.04	0.36 ± 0.06

The stress-strain curves offer the information of compressive behaviour to understand the mechanical performance of materials when exposed to high

temperature. According to the curves, at room temperature (25 °C), the curves performed perfect linear relationship between stress and strain until the samples failed, which means all four controlled cements pastes (OPC, HYC, HYP and FAN) exhibited linear elastic behaviour characteristic of brittle materials.

When materials were exposed to higher temperatures (400 and 600 °C), the stress-strain curves obtained were essentially the same of its initial straight-line portion comparing to the curves at room temperature. However, after yield point has been reached, the strain increases faster than the stress until rupture occurs. The elastic zone is delimited by the yield point; materials underwent plastic deformation until it broke (OPC, HYC and HYP specimens). When the 0.2% yield strength offset criterion is satisfied, the stress-strain curves indicate that selected pastes have plastic behaviour and equations derived for linear elastic behaviour cannot be more used. Hence the representation in previous figures is only indicative of the behaviour of materials and useful to compare the different performance between them.

On the other hand, the curves of FAN pastes exhibited approximately linear behaviour at 400 and 600 °C, which there are almost no plastic deformation until the final failure. Particularly noteworthy is the fact that before the failure, larger deformation (values of strain) happened to FAN along with higher stress.

Figure 6.2.5 Strain changes before running test when the specimens were heated up to 1000 °C under a 5±1 N load.

At temperature of over 800 °C (800 and 1000 °C), Portland cement and two hybrids cements exhibited ductile behaviour with permanent deformation. Their ultimate limit stress declined with much larger deformation. Meanwhile, the yield stress values are quite small for them with nearly negligible elastic deformation (see Table 6.2.1-6.2.4). For alkali-activated cement FAN, the yield stress of declined dramatically when exposed over 800 °C. This material started to soften over 800 °C and exhibited pseudo-plastic behaviour without final failure. Fig.6.2.5 plots the strain changes versus time before running the cross-head. It is clearly showed that a huge deformation ($\approx 60\%$ strains) happened under a 5 ± 1 N load, which were soften too much to determine compressive strength. Another conclusion could be archived is that hybrid cements exhibited more similar to OPC rather than FAN (softening behaviour) at higher temperature.

Figure 6.2.6 Plot of σ_y / σ_u and ϵ_y / ϵ_u ratios versus temperature.

The yield strength σ_y is the stress at which plastic deformation becomes noticeable and yield is initiated. Therefore it is the stress that divides the elastic and plastic behaviour of the material (Timoshenko and Young 1956). In this study, the ultimate strength σ_u was recorded before the materials break or when the materials break (not all cases, except OPC at 1000 °C, FAN at over 800 °C).

At room temperature, yield strength could be assumed equal to ultimate strength and breaking strength with nearly negligible deformation. The ratios of σ_f / σ_u and ϵ_y / ϵ_u are equal to 1, which indicate that the materials performed perfect brittle behaviour. With temperature increasing, the ratios of σ_f / σ_u and ϵ_f / ϵ_u declined. This could indicate that the materials behaviour transitioned from

brittle to non-brittle with permanent deformation before they failed. The ratios of σ_y / σ_u and ϵ_y / ϵ_u are plotted in Fig.6.2.6. Unlike OPC and FAN, two hybrids cement HYP and HYC started to exhibit as non-brittle failure material at 400 °C, which underwent more plastic deformation before they broke.

Figure 6.2.7 Physical appearance of OPC, HYC, HYP and FAN specimens after compression test at evaluated temperature.

Fig.6.2.7 depicts the physical appearance of tested specimens after testing at evaluated temperature. From the image, obvious changes were obtained for the materials exposed to evaluated temperature. In hybrids cement pastes (HYC and HYP) and FAN paste, a progressive lightening of the original dark grey colour was apparent after at 400 °C and 600 °C. Heating up over 800 °C caused abrupt changes to a brick-red-orange colour for HYP and FAN. The colour change for HYC over 800 °C was lighter than HYP and FAN pastes. With the OPC reference paste, very little changes in the paste colour were noted even after exposure at 800 °C. The similar colour changes of alkali-activated fly ash paste were recorded by other study ([Fernández-Jiménez, Palomo et al. 2008](#), [Donatello, Kuenzel et al. 2014](#), [Martin, Pastor et al. 2015](#)). The behaviour is characteristic of changes in iron oxide compounds present in fired FAN pastes and the process is analogous to that in the brick industry ([Trindade, Dias et al. 2009](#)). The results in this study agree well with former study. Chemical composition of raw

materials (Chapter 4, section 4.2) showed that the Fe_2O_3 composition is 7.23%, 4.93% and 3.83% for FA, HYP and HYC respectively. That can explain the intense of colour changes which were obtained visually: $\text{FAN} > \text{HYP} > \text{HYC}$.

Figure 6.2.8 Sketch diagram for pastes samples after in-situ high temperature compression test.

Fissures were noted in the tested samples (see Fig.6.2.7). A simple draft of testing sample was illustrated in Fig.6.2.8. The fissures caused by compression test are mainly of shear fracture (see Fig.6.2.8 (a), (b) and (c)) however with varying degree of deformation according to exposure temperature. For the sample FAN paste, after testing at 1000 °C, it was flattened without failing, generating a *barrel* effect ((see Fig.6.2.8 (d)) (Martin, Pastor et al. 2015).

Figure 6.2.9 Compressive strength and strain versus temperature.

The in situ compressive strength and strain (yield strength and strain) results versus temperature of selected materials are plotted in Fig.6.2.9. As expected, Portland cement performed well at ambient temperature, and then followed by HYC and HYP. Alkaline cement FAN exhibited low initial compressive strength under this test condition.

The materials OPC, HYC and HYP underwent a reduction of compressive strength up to 600 °C. From ambient temperature to 400 °C, HYC performed more stable than the other two binders. Between 400 and 600 °C, the decline of strength of materials was more quick and abrupt, in another word, it indicated that exposure up to 600 °C, and the binders lost their strength. Opposite performance was observed in alkaline cement FAN, with evaluated temperature (400 to 600 °C), compressive strength values rose significantly, especially at 600 °C with large deformation and linear elastic behaviour.

When exposure temperature is over 800 °C, the compressive strength for all materials declined to lower value with small yield strain. However, two hybrid cements remained higher strength when compared to Portland cement. Alkaline activated cement FAN, at higher temperature, from 800 to 1000 °C, its behaviour was plastic with lower yield stress, and at 1000 °C, the pastes softened with 5 ± 1 N pre-load as mentioned before.

6.2.2 Fracture behaviour

The fracture behaviour was studied using TPB (three point bending) tests performed on smooth and SELNB (Single edge V-notched beam) specimens to obtain flexural strength and fracture toughness, respectively. Subsequently their fracture surface was analysed. Such tests were conducted in air atmospheres over a temperature range from ambient temperature (25 °C) to 600 °C with the condition explained in section 3.2.

- **Flexural strength.** The TPB test results for smooth samples and specific measurements of each specimen were used to calculate σ - ϵ curves applying the Euler-Bernoulli equations (eq.3.3, eq. 3.4) σ - ϵ curves were plotted for each material with different temperature. Then the average flexural strength values with their corresponding standard error are plotted along with the studied temperature range for all the tests. The curves are considered to exhibit ductile behaviour when the 0.2% yield strength offset criterion is satisfied. The modulus of elasticity was found

from the slope in the elastic zone on the stress-strain curves obtained in the bending tests at different temperature.

- **Fracture toughness.** The TPB test results for the SELNB specimens and the specific measurements of each sample were used to calculate the resultant fracture toughness by applying eq. 3.6. The flexural force-displacement curves obtained from each temperature are plotted in some case. According to the fact that cementitious materials are very brittle, all the curves show similar trends. Afterwards, the average fracture toughness with its corresponding standard error is shown for the studied temperature range for all materials.
- **Fracture surfaces.** After the TPB tests, fracture surfaces was analysed with SEM, selected points with EDX are presented. For different materials, surfaces at 25, 200, 400, and 600 °C are shown. The microstructure was analysed to track the fracture behaviour, especially on the cracks and pores.

6.2.2.1 Flexural strength

Then bending test stress-strain curves are shown in Fig.6.2.10. The curves showed linear elastic behaviour for all materials when the exposure temperature at 25, 200 and 400 °C. Although in some samples, the curve is not perfect linear (the part before the materials breaking) and performed plastic behaviour, the strain is not satisfying 0.2 % yield strength offset. At this temperature range, the materials exhibited brittle failure as in the compression trials. At 600 °C, mechanical strength was negligible in Portland cement OPC, the specimens collapsed before the value could be determined. Same resulted was achieved by the former research by A. Martin (2015). Two hybrids cements exhibited similar behaviour; the bending strength of HYC and HYP continued to decline when exposed to 600 °C, meanwhile non-linear behaviour was observed to follow the first linear stage. HYC performed higher bending strength than HYP. HYP exhibited lowest bending strength in all materials; however it could be tested at 600 °C, which means at 600 °C, HYP maintained strength when comparing with OPC. The alkali-activated FAN paste exhibited plastic behaviour after it reached yield point with lager deformation. The yield strength of FAN declined with rising temperature.

Classic bell shape curves are typical obtained in cement-based materials (mortar, concrete etc.) (Nallathambi, Karihaloo et al. 1984, Sih 1984, Swartz and Yap

1986, Elices and Planas 1996, Djaknoun, Ouedraogo et al. 2012). In TPB tests, this type of curves indicates the crack evolution according to the reference: in the first linear stage, the cracks appeared but do not extend, in the non-linear stage to the peak of load, the fracture process grows, and propagation of cracks and micro-cracks occurred. The third stage was called strain softening zone following by rapid crack growth. In this study, some bending stress-strain curves exhibited quasi-bell shape evolution, after the materials fail, unstable data was recorded (see Fig.6.2.10, OPC curve at 400 °C, HYC curve at 400 °C etc.). The quasi-bell shape of stress-strain curves could be explained by the former two stages in the reference to describe the cracks evolution in this study. With temperature increasing (especially up to 400 °C), more micro-cracks appeared in the materials and could be spread, which lead to the loss of strength.

Figure 6.2.10 In situ flexural stress-strain curves at different temperatures of OPC, HYC, HYP and FAN.

In Table 6.2.5, the modulus of elasticity of each material versus temperature was listed. At room temperature, OPC has highest elastic modulus, and then followed two hybrid cements HYC and HYP, Alkaline cement FAN is lower than the other three materials. The result is agreed with the mechanical (compressive and flexural) strength of 28-day pastes in former test.

Table 6.2.5 The modulus of elasticity at high temperature for materials (mean value $\pm$ standard error).

Pastes	OPC	HYC	HYP	FAN
T(°C)	E(MPa)	E(MPa)	E(MPa)	E(MPa)
25	14.58 $\pm$ 0.27	13.96 $\pm$ 0.59	11.54 $\pm$ 1.63	8.14 $\pm$ 0.45
200	4.66 $\pm$ 0.72	5.86 $\pm$ 0.41	3.80 $\pm$ 0.15	5.21 $\pm$ 0.05
400	4.27 $\pm$ 0.35	4.91 $\pm$ 0.24	3.01 $\pm$ 0.47	5.71 $\pm$ 0.20
600	-	3.15 $\pm$ 0.20	2.11 $\pm$ 0.21	4.28 $\pm$ 0.31

In Fig.6.2.11 (left), the relative variations at evaluated temperature for each material was plotted in which the modulus of elasticity for ambient temperature was assigned a value of 1. As noted, the OPC and HYP underwent greater deterioration when exposure to 400 °C (lost nearly 70%) with temperature. HYC performed a little better than OPC and HYP. FAN behaved best with fewer declines up to 400 °C. At 600 °C, the modulus of elasticity of OPC declined steadily nil. HYC and FAN pastes behaved similarly to decrease as OPC but better than OPC. The values of elastic modulus for HYP performed difference behaviour; it increased slightly at 600 °C. The reason is not clear but could be due to the composition of fly ash content. From the aspect of elastic modulus, hybrid cements and alkaline cement (here is alkali-activated fly ash) performed better at high temperature than OPC.

The average flexural strength of testing materials is given by Fig.6.2.11 (right). At room temperature, HYC performed better than the other materials with nearly 6 MPa of bending strength at the same testing configuration. HYP had lowest values of bending strength among all materials (around 3 MPa). At high temperature until 400 °C, OPC, HYC and HYP exhibited similar declines; HYC still performed best resistance as temperature. The bending stress of FAN increased between 200 and 400 °C, similar behaviour was reported by the same group (Fernández-Jiménez, Palomo et al. 2008). At 600 °C, OPC lost too much bending strength to be tested, HYP had quite small value, and the phenomenon was corresponded to the results of elastic modulus. Alkaline cement FAN values came from yield stress, due to this material underwent large deformation at 600 °C.

Figure 6.2.11 Relative modulus of elasticity at different temperature (left); In-situ three-point bending tests at different temperature (right).

Figure 6.2.12 Specimens before and after in situ bending tests at different temperature.

Specimens changes before and after in-situ bending tests are illustrated in Fig.6.2.12. It noted that, OPC specimens cannot be tested at 600 °C because the materials started to collapse. Two hybrid cements, HYC and HYP, behaved similarly at 25, 200, 400 and 600 °C with brittle failure. Alkaline cement FAN underwent colour change from room temperature to high temperature, which is similar to the compression test. At 600 °C, it still performed partial elastic behaviour until it fail to two halves. However, above 600 °C; permanent deformation appeared (at 700 and 800 °C). After such significant deformation, the bending strength declined to nearly negligible due to micro-cracking across

the entire surface, although they did not split into two halves. The difference between two temperatures is the macro-crack appearance. At 700 °C, macro-cracks were obviously observed around the surface but not appeared when this material exposed to 800 °C.

6.2.2.2 Fracture toughness K_{IC} of selected materials

Fracture toughness K_{IC} is the critical value of the stress intensity factor at a crack tip needed to produce catastrophic failure under simple uniaxial loading. The subscript I in K_{IC} means that this critical stress intensity factor, K , refers to mode I fracture at the crack tip (Elices and Planas 1996, Sukontasukkul, Pomchiengpin et al. 2010, Djaknoun, Ouedraogo et al. 2012, Sarker, Haque et al. 2013). It has been mentioned before that although the fracture toughness for cement-based materials is not used as a design index, it makes sense to study the fracture behaviour of cementitious materials. Especially when cementitious materials are exposed to high temperature (e.g. fire accident), fracture behaviour study is necessary. In this Ph.D. work, the fracture toughness K_{IC} was used to comparing the fracture behaviour of different materials at evaluated temperature.

The three-point bend single edge notched beam is a useful configuration for fracture toughness testing since it can be easily shaped and tested. In chapter 3, the specimen preparation progress and V-notch introduction method were explained in detail.

Need to be illustrated that the specimens size, $50 \times 14 \times 4$ mm (length $\times$ width $\times$ height), and supporting distance (span), 20 mm are non-standardized geometries. In all international standards for fracture toughness testing, the span-to-depth ratio is fixed to a value of 4 (ESIS, 1992; RIMEM, 1985; ASTM, 1993a, b). In our case, the span-to-depth ratio was designed as 5 and the crack-to-depth ratio was designed as 0.375 with the consideration of sample preparation and testing machine configuration (e.g. the size of oven). Therefore the stress intensity factor for calculating fracture toughness was used expressions proposed by G.V. Guinea et al., in 1998 (Guinea, Pastor et al. 1998), which can be used for any value of the crack-to depth ratio and span-to-depth ratio larger than 2.5. The formula was introduced in section 3.3.2.3.

Figure 6.2.13(a) Broken specimens of HYP paste after introduce notches; (b) Micrograph of the notches introduced to testing specimens.

Figure 6.2.14 (a), (b) and (c) Toughness displacement-load curves versus temperature for OPC, HYC and FAN; (d) Fracture toughness versus temperature.

HYP was failed to introduce V-notch in the first step, the reason could be explained by lowest bending strength behaviour of this materials (around 3 MPa). Fig.6.2.13a showed broken specimens of HYP after introducing notches. The micrograph shows a very sharp V-notch (around 10 μm) which was successfully introduced to pastes (see Fig.6.2.13b).

The in situ fracture toughness displacement-load curves for each material were plotted in Fig.6.2.14 (a, b and c). For reference OPC and hybrid HYC performed brittle behaviour at all testing temperature. The difference was recorded in the test of FAN at 400 and 600 $^{\circ}\text{C}$, the testing curve exhibited a small displacement-load tail after the sample fail. It could indicate that alkaline cements FAN was tougher than the other two materials at higher temperature. Inasmuch as the specific fracture energy was larger than the other two materials when the load tends to zero.

Brittle materials have small K_{IC} values and are liable to catastrophic failure, in which the plastic strain at the tip of the crack is nil or negligible. Fig.6.2.14d showed the K_{IC} values versus temperature for tested materials. The K_{IC} values were very low, as expected, for all materials tested (0.2-0.3 $\text{MPa m}^{1/2}$). From ambient temperature to 400 $^{\circ}\text{C}$, OPC and HYC performed similar behaviour with slightly value decline. OPC, toughness fell at temperatures of over 400 $^{\circ}\text{C}$. In contrast, FAN toughness increased slightly when temperature up to 400 $^{\circ}\text{C}$. During thermal treatment was going up to 600 $^{\circ}\text{C}$, OPC specimens started to lose the strength under 2-3 N pre-load, which couldn't be tested. By contrast, from 400 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$, hybrid cement and alkali cement exhibited similar performance with clearly increase of K_{IC} values.

6.2.2.3 Fracture surface

After fracture toughness test, half sample was selected at each temperature for SEM study. The fracture surface of sample was covered by Au and then characterized by SEM. According to the fact that it was failed to introduce notches to HYP matrix, the half sample from flexural test by TPB was selected and analysed for fracture surface.

Figure 6.2.15 Fracture surface of OPC after three-point bending test for the measurement of the fracture toughness at 25 and 400 °C. The loading direction was parallel to the fracture surface.

Figure 6.2.16 Fracture surface of HYC after three-point bending test for the measurement of the fracture toughness at 25, 400 and 600 °C. The loading direction was parallel to the fracture surface.

Figure 6.2.17 Fracture surface of HYP after three-point bending test for the measurement of the flexural strength at 25, 400 and 600 °C. The loading direction was parallel to the fracture surface.

Figure 6.2.18 Fracture surface of FAN after three-point bending test for the measurement of the fracture toughness at 25, 400 and 600 °C. The loading direction was parallel to the fracture surface.

SEM characterization of the fracture surfaces has been carried out to identify the fracture mechanisms for each material in Fig.6.2.15-6.2.18. All images were organized parallel to the direction of load (up-to-down). Notch root was marked in the graph due to it was clearly tracked. Above the notch root, fracture surface was graphed and under the notch root in SEM images it showed the notch surface introduced before the test. In addition, the surface cracks on the specimens (Fig.6.2.15c) exhibited properties of semielliptical surfaces cracks. The cracks propagated from the centre of zone of pores and towards to the rest of material.

SEM investigations of OPC are shown in Fig.6.2.15. Typical failure surface of brittle materials was identified. At 25 °C (Fig.6.2.15a), a compact typical hydrated cement pastes structure was observed, no obvious surface cracks in this material. The failure was caused by main extending crack of the notch. The distinct change in fracture surface of sample at 400 °C is propagation of the cracks through the entire matrix. These cracks lead to loss of strength of materials.

Two hybrids cements showed similar fracture surface of brittle materials like OPC. At room temperature, more pores than OPC materials were observed through the matrix surface, which explained lower compressive strength of HYC and HYP. At high temperature (400 and 600 °C, see Fig.6.2.16b, c), the surface of HYC had no clearly identifiable cracks, in contrast HYP shows clearly propagation of cracks with temperature. SEM investigation of HYP showed hills-like surface due to without introducing notches (see Fig.6.2.17).

Figure 6.2.19 Micrographs of FAN paste before (left) and after exposure to 600 °C (right) after three-point bending test for the measurement of the fracture toughness.

According to the SEM images, material FAN exhibited more obviously porosity changes with temperature. In Fig.6.2.18, we can obtain with temperature increasing; the porosity of the fracture surface has been increased. Some cracks appeared between pores and some of them connected. In Fig.6.2.19, micrographs of FAN paste at room temperature and after exposure 600 °C were presented. The N-A-S-H gel distributed in the matrix at room temperature exhibited morphologically varies. After 600 °C, eggshell-like gel spalled from unreacted fly ash particles and the matrix looked less cohesive, which would explain its lower mechanical strength at 600 °C.

6.3 Physicochemical behaviour of materials after post-thermal tests

In section 6.2, In-situ high temperature mechanical behaviour of each material has been discussed. In this section, post-thermal behaviour of selected materials is studied. The objective is to compare post-thermal properties of different type of binder material after high temperature exposure.

All pastes were weighted, measured prior to being exposed to high temperature which has been introduced in section 3.2 for a period of two hours. Immediately after removing from the oven, half of each samples batch was left to cool on a ceramic plate in air and the other half was cooled by immersion in to water for 15~20 minutes then left to dry on paper towels in air.

6.3.1 Visual changes in paste sample

The Fig.6.3.1-6.3.2 shows the pastes sample after exposure to 800 °C and 1000 °C, which were cooled by water immersion or air convection after removing from the oven. The most interesting fact is that OPC pastes which cooled in water lost their integrity and become powder. This phenomenon happened very fast when the pastes contact with water. In real life, most fires are extinguished with water and the subsequent rehydration of the fire damaged cement based materials is a particular concern.

Hybrid cement HYC and HYP exhibited better thermal resistance especially cooled in water immersion. After exposed to high temperature (800 and 1000 °C), both cements remained their stability, and obvious visual cracks of sample

surface did not appear. When put the hot samples of HYP into water, there were paste particles which spalled from the surface.

Figure 6.3.1 Paste samples after exposure to 800 °C and cooling by water immersion and air convection, OPC and HYC samples were photographed inside water HYP and FAN samples were photographed after removing from water.

Obvious shrinkage behaviour and macro-cracks were obtained in FAN pastes. Colour changes appeared the same as that happened in former in-situ mechanical tests. At 800 °C, macro-cracks were more observed in water cooling process than it in air. When exposed to 1000 °C, much more macro-cracks were visibly graphed. Behaviour of FAN pastes is interesting at high temperature is that when samples were put into water; they remained integrity although with lot of macro-cracks.

Figure 6.3.2 Paste samples after exposure to 1000 °C and cooling by water immersion and in air convention. OPC and HYC samples were photographed inside water, HYP and FAN samples were photographed after removing from water.

6.3.2 Length and weight changes in prismatic pastes

After thermal treated at target temperature, the samples were cooled in two different methods. After cooling, each sample was reweighted and measured before mechanical tests.

The length and weight changes in prismatic pastes were plotted in Fig.6.3.3 and Fig.6.3.4. Exposure at under 600 °C, OPC, HYC and HYP exhibited stable dimensions over this temperature range when cooled in water but a steady shrinkage when cooled in air. The tendencies suggest that the expansion caused by rehydration by water was sufficient to compensate for thermal shrinkage caused by the initial dehydration reactions. In contrast, FAN showed totally the same dimensions both in water and air cooling circumstance. In general, the cooling method had no dramatically influence on the pastes when heated to 600 °C. After heating above 600 °C, all the four material pastes exhibited larger length change. OPC pastes lost dimensions stability and the pastes vanished fast in water at both 800 and 1000 °C; this behaviour could indicate that the expansion caused by the rehydration of free lime by cooling water destroyed this material.

Figure 6.3.3 Change in pastes length as a function of temperature exposure and cooling method, A- cooled in air; W- cooled in water.

Between 600 and 800 °C, two hybrids cements HYC and HYP, and the alkaline cement FAN exhibited clearly a major shrinkage event. Especially in FAN pastes. The reason should be explained by sintering process happened in alkaline

cement FAN (Dombrowski, Buchwald et al. 2007, Rickard, Temuujin et al. 2012). The former research found that the high alkali content of fly ash-based binder favored the formation of a molten phase at temperatures of around 600-to-700 °C (Fernández-Jiménez, Palomo et al. 2008). From 800 to 1000° C, these three materials exhibited similar trends with expansion behaviour.

The weight losses of pastes were plotted in Fig.6.3.4. OPC, HYC and HYP performed more weight losses (nearly 25%, 24% and 27%, respectively) than FAN pastes (13%) after 1000 °C exposure. This three materials exhibited similar behaviour from 25 °C to 400 °C with dominant weight loss. In this temperature range, weight loss mainly related to the loss of free and bound water (in gels and hydrates) (Maravelaki-Kalaitzaki, Bakolas et al. 2003, Stepkowska, Perez-Rodriguez et al. 2003, Alonso and Fernandez 2004, Stepkowska, Blanes et al. 2004). It could reveal that the water content in alkali-activated FAN pastes is less than OPC and hybrids cement.

Figure 6.3.4 Change in pastes weight as a function of temperature exposure and cooling method, A- cooled in air; W- cooled in water.

All the samples cooled in water showed less weight loss, two reasons probably could explain it. One is the rehydration process occurred in pastes when the samples were put into water, this happened especially to OPC, HYC and HYP. From Fig.6.3.4, it clearly to observed that in OPC, HYC and HYP, the samples cooled in water lost less weight due to rehydration process. The other explanation is free water absorbed in pastes. In FAN samples, the second process happened dominantly due to it is different to rehydrate with water for FAN pastes. After 400 °C and 600 °C exposures, the differences of weight losses in FAN between water and air cooling are very small and could be ignored. At 800 and 1000 °C, cooled in water had less weight loss than in air due to more crack generated in the pastes when put the sample in the water (see Fig.6.3.2, sample FAN 800 °C in water and air). The cracks let more water absorbed.

The data for HYP at 800 °C in water was not credible (see Point A in Fig. 6.3.4). Because when the samples were removed from the oven and put into water, severe spalling happened to the sample which introduced in former section (see Fig.6.3.2, sample HYP 800 °C in water and air), the loss of pastes particle dramatically influenced the results.

6.3.3 Mechanical strength after heat exposure

The samples were finally tested in mechanical strength (compressive and flexural) after cooling to ambient temperature according to the standard UNE-EN 196-1 though two machines (Netch-401-2 and Ibertest Autotest 200-10, see Fig.3.2.3). The details were introduced in section 3.2.

Fig.6.3.5 plots the compressive strength of each material after thermal treatment at target temperature by different cooling methods. In this case, the materials were located directly in the furnace without pre-loading; it could be tested after heating until 1000 °C comparing with in-situ mechanical tests.

The initial compressive strength of OPC is really higher than the other cements as expected. However, with the increase of temperature, the strength declined dramatically. Hybrid cements and alkaline cement were obtained more stable behaviour than OPC when exposed over 600 °C. FAN performed different compressive behaviour when compared with OPC, HYC and HYP. After 800 °C, FAN showed best strength values then the compressive stress declined after 1000 °C.

The flexural strength of each material after thermal treatment at target temperature by different cooling methods was illustrated in Fig.6.3.6. After 400 °C exposure, Portland cement OPC almost loses the flexural strength to very low value. The decline was remarkable even though it has highest flexural strength without high temperature exposure. Two hybrid cements were obtained similar behaviour with a slightly increase between 400 and 600 °C. And then the flexural strength declined again until high temperature (1000 °C). FAN exhibited different behaviour in both cooling methods. In general, alkali cement FAN showed better residual values with high temperature.

Figure 6.3.5 Compressive strength of each material versus temperature as function of cooling method (A- cooled in air; W- cooled in water). Note that results are the average of eight measurements for compressive strength.

Figure 6.3.6 Flexural strength of each material versus temperature as function of cooling method (A- cooled in air; W- cooled in water). Note that results are the average of four measurements for flexural strength.

The residual flexural strength of each material is plotted in Fig.6.3.8. Portland cement exhibited lowest strength resistance with temperature among all materials, after 400 °C, OPC lost its strength same as in situ bending test. Between 400 and 600 °C, hybrids cements HYC and HYP exhibited similar behaviour with increasing of bending strength then from 600 to 800 °C declined in strength. FAN paste exhibited slightly drop between room temperature to 400 °C, then performed dramatically decline in bending strength between 400 and 600 °C. From 600 to 1000 °C, the values increased. The value at 1000 °C cooled in air exhibited quit high, the reason could be due to the effect from shrinkage on bending test.

The behaviour of sample cooled in water represents similar behaviour of residual compressive and bending strength. Attention should be payed is that when cooling directly in water made OPC pastes breakdown at 800 and 1000 °C. Quick water contact also declined the bending strength of FAN materials. From

this aspect, hybrids cement own better mechanical resistance at high temperature. In tow hybrid cements, HYC exhibited better mechanical performance than HYP in situ and residual strength after thermal treatment.

Figure 6.3.7 Residual compressive strength after two-hour exposure to different temperature as function of cooling method (A- cooled in air; W- cooled in water).

Figure 6.3.8 Residual flexural strength after two-hour exposure to different temperature as function of cooling method (A- cooled in air; W- cooled in water).

6.4 Microstructure and Mineralogical characterisation of materials after exposure to high temperature

Cement hydration process is a very complex phenomenon. In chapter five, microstructure and mineralogical characterisation of the four studied binder materials has been investigated. For Portland cement paste (OPC), calcium silicate hydrate, C-S-H gel is the main hydrate production; a mix of cementitious gels (N, C)-A-S-H+C-(A)-S-H + C-A-S-H is considered to be main hydration

products for hybrid cement HYC (Qu, Martin et al. 2016) and HYP; For FAN pastes, the main reaction product is N-A-S-H gel. Gel phases are principally responsible of the cement materials resistance so that their appearance and evolution upon time is of the utmost importance.

This section is focus on microstructure and mineralogical evolution with temperature, particularly in high temperature ($> 600\text{ }^{\circ}\text{C}$), which is important and may explain the materials macroscopic behaviour of cement-based materials.

6.4.1 Pore structure study by MIP

Mercury intrusion porosimetry (MIP) was used to investigate the pore structure evolution of selected pastes after high temperature exposure. For OPC hard pastes, rapid increase of the porosity happened at temperature higher than $500\text{ }^{\circ}\text{C}$ due to dehydration of Portlandite and decomposing of C-S-H gel (Zhang 2013). Former investigation (Martin, Pastor et al. 2015) showed that most prominent changes on pore size distribution were observed at 600 , 800 , and $1000\text{ }^{\circ}\text{C}$ when the group studied mechanical behaviour of alkali-activated aluminosilicates at high temperature. In this study, paste samples with thermal treatment at temperature higher than $600\text{ }^{\circ}\text{C}$ were analysed by MIP to determine the pore volume and its size distribution.

Figure 6.4.1 Variation in porosity of four materials with temperature.

In Fig.6.4.1, the plot of total porosity has been presented. Generally speaking, for OPC, HYC and HYP pastes, total porosity values increased with temperature, although between 800 and $1000\text{ }^{\circ}\text{C}$ OPC turned slightly downward. FAN

performed more stable in total porosity until 1000 °C, which could be related to its mechanical behaviour.

Log differential intrusion volume against pore diameter ($dV/d\log D$) is showed in Fig.6.4.2. The peaks represent the pore diameters corresponding to the highest rate of mercury intrusion per change in pressure (Zhang 2013). This pore diameter was called critical pore size, which means where the pores begin to percolate. Here we used it to study pore size distribution of materials.

Exposure to high temperatures did seem to have a significant effect on pore size distribution. After exposure to 600 °C, the prominent changes were observed. The pore size distribution of OPC, HYC and HYP exhibited similar behaviour when exposure temperature increases. Large capillaries with size around 1 μm become dominant pores in the material after 1000 °C thermal treatment. The pore size distribution at 800 °C for this three pastes were obtained two main distribution peaks with different size (0.1-0.2 μm and 0.9-1 μm for OPC, 0.1-0.2 μm and 1-2 μm HYC, 0.3-0.4 μm and 1-2 μm for HYP). This might be caused by random micro-cracking of the microstructure.

Figure 6.4.2 Pore size distribution of cement pastes: OPC, HYC, HYP and FAN before and after high temperature exposure.

Unlike OPC binders, the fly ash materials were found to recrystallize after initially decomposing (reference). In-situ mechanical test revealed that between 600 to 800 °C, FAN exhibited pseudo-plastic behaviour due to formation of a sintering phase. This new phases become more fluid, with sufficient time (in our case, two hours thermal treatment), they were able to repaired the flaws and cracks present in the materials. It would be explained the size distribution of FAN changed to smaller from 800 to 1000 °C.

Figure 6.4.3 Total pore volume segmented into different size range for selected pastes: OPC, HYC, HYP and FAN before and after high temperature exposure.

Fig.6.4.3 exhibited the total pore volume of pastes at evaluated temperature, along with segmentation of the total pore volume into three size ranges according to IUPAC recommendation (Rouquerol, Avnir et al. 1994): 0.0066-to-0.05 μm, 0.05-to-0.2μm, and > 0.2μm. The smallest pore size group of IUPAC classification is 0.002-to-0.05μm, but according to the fact that the detection limits of 0.0066 μm for our MIP instrument, in this study, it is defined as 0.0066-to-0.05μm. The smaller sized pores (0.0066-to-0.05μm) represent the pores in the reaction product in the binder systems (Dakhane, Tweedley et al.

2017), the larger size pores are attributed to the space between the reaction products as well micro-cracks. The study of three size ranges could offer information of reaction product with temperature and also cracking properties of materials. For OPC, and two hybrid cements HYC and HYP, the segmentation of total pore volume showed similar trends with increasing of temperature. The smaller sized pores (0.0066-to- 0.05 μm) declined until the pastes exposed to 600 °C and almost cannot be tested after exposure to 800 °C. This change could illustrate that the changing of reaction products in the binder with temperature. The volume of larger pores increased with temperature, due to the cracks in the binder and increasing spaces between the reaction products, which detrimentally affects the strength of the binder. FAN pastes presented distinguish changes of pores volume, after high temperature 1000 °C, the overall pore volume gained due to the increasing of total three range of pores volume, which could explain the high compressive strength of FAN pastes after exposure to high temperature.

6.4.2 XRD analysis

From the physical behaviour presented and former study, examination of four material pastes chemistry and mineralogical at temperature exposures above 600 °C, is of considerable interest. Fig.6.4.4 shows the XRD patterns for reference material OPC. The 28 days pastes were exposed to different target temperature.

The Fig.6.4.4 first shows the trace for 28 days paste of OPC without heat treat and then for the same materials after exposure to high temperature (600, 800 and 1000 °C, cooled in air). In the initial pastes at 28 days, typical hydration products C-S-H gel was detected which related to a halo between 20-35°. Other important peaks are due to portlandite, ettringite, calcite and some unhydrated alite and belite.

After heating 600 °C, some reflections disappeared. A progressive reduction of the intensity of the peak to portlandite is noticed. According to the results of DTA, the breakdown of portlandite of this sample happened at around 436 °C. The detected small peaks of portlandite probably come from 1) the rehydration process when the sample was cooled in air; 2) un-decomposed portlandite in pastes when exposed to 600 °C. Ettringite is not present due to this crystalline phase is not stable when exposed to 100 °C (decomposing). The other study indicated that (Alonso and Fernandez 2004) the dehydration and transformation of C-S-H gel started at around 450 °C OPC materials lose its strength and started

to burst in the in-situ trials between 400 and 600 °C, which was possibly caused by water evaporates.

When exposed to higher temperature (800 and 1000 °C), the reflection peaks of calcite practically disappear. Lime is also well identified in the pastes heated at and above 800 °C, which come from portlandite and calcite transformation. Effectively, in the section 6.4.5 these processes were observed by DTA. The curve of DTA shows the decarbonation of calcite happened at around 690 °C, which also confirmed by the others.

The brownmillerite, larnite are also present. According to XRD, brownmillerite is probably come from the raw material and seem to be stable respect to high temperature (the intensity has no clearly changed). However with respect to C_2S (larnite), increase of intensity of related peaks has been observed at 800 and 1000 °C. They could come from some C_2S from unhydrated OPC, as well come from the formation of new C_2S in high temperature. It is impossible to distinguish by XRD its proportion.

Legends:

- A:**Alite, C_3S , 031-0301;
- Al:** C_3A 032-1048;
- An:**Anhydrite, $CaSO_4$, 074-2421;
- B:**Larnite, C_2S , 033-0302;
- C:**Calcite $CaCO_3$, 083-0578;
- E:**Ettringite, 041-1451;
- F:**Brownmillerite, $Ca(Al, Fe)_2O_5$, 030-0226;
- P:**Portlandite, $Ca(OH)_2$, 044-1481;
- G:**Gypsum, $CaSO_4 \cdot 2H_2O$, 037-1496,
- I:** Lime, CaO , 074-1497

Figure 6.4.4 XRD data of OPC pastes before and after selected treatments.

XRD data for hybrid cement HYC pastes before and after heat treatment are included in Fig.6.4.5. The diffractograms of 28 day samples contained a hump (colour marked) from 25 to 35° which, as discussed in chapter 5, was associated with the possible formation and precipitation of a mix of C-S-H, C-(A)-S-H / C-A-S-H gels. Portlandite, ettringite, calcite and carboaluminates appeared as new hydration phases. Mullite and quartz which come from raw fly ash components were also detected.

Figure 6.4.5 XRD data of HYC pastes before and after selected treatments.

When the sample was exposed to 600 °C, the presence of ettringite and portlandite disappeared. There are no new phases formed at this temperature. Calcite, mullite and quartz are still detected. Calcite does not decompose under 600 °C and the other two phases come from fly ash component. The presence of a halo associated with the formation of mixed gels (colour marked, 25-35° 2θ) is still visible, although the intensity has declined, which probably indicate that when heating up to 600 °C the gel could still remained thermally stable.

At heating to 800 °C, peaks related to new crystalline phases were detected. The phase α' -Ca₂SiO₄ appeared. Another new crystalline phase noted at 800 °C is gehlenite. Mullite and quartz still be remained as phases coming from fly ash. The amorphous hump appeared at room temperature and 600 °C related to hydration products changed significantly. This phenomenon may related to phase transformation when the temperature between 600 °C and 800 °C. Calcite decomposed without any related peaks.

When heating temperature increased up to 1000 °C, α' -Ca₂SiO₄ likewise decomposed and new phases appeared: Rankinite, wollastonite, pseudowollastonite. The intensity of gehlenite improved as new phase which often found in recrystallized blast furnace slag. Appearance of anhydrite at 400, 600 and 800 °C disappeared at 1000 °C.

It is clearly noted that changes in crystalline phases happened after exposure to 600 °C. After 600 °C, the intensity of peaks in HYC pastes declined, this could be related to transformation of crystalline phases. Also the totally decomposing of mixed of gels happed after 600 °C exposure. The strength of HYC declined after 600 °C exposure which could be realted to this phenomenon.

The Fig. .6.4.6 included XRD patterns for HYP pastes before and after high temperature exposure. The hydrated hybrid cement HYP paste is discussed in former chapter. The main hydration product is C-(A)-S-H, C-A-S-H and (N, C)-S-H-like mix of gels. Ettringite and calcite precipitated as second products. Prior to high temperature exposure, the HYP paste was completely free of portlandite. In DTA results, typical peak around 436 °C associated with the portlandite dihydroxylation did not appear in HYP. It confirmed the fact of there is no portlandite. Mullite and quartz come from the initial fly ash component were detected as well.

XRD data of paste at 600 °C exhibited similar pattern as non-fired samples, the difference is the absence of ettringite and detected anhydrite. The other visible change is the decline of intensity of patterns, which could be explained that decomposition of gel happened.

The most distinguished result in XRD pattern was recorded after heating of 800 °C. Peaks associated to calcite disappeared. A group of calcium silicate type phases was noted. Grossular, gehlenite and larnite appeared as the main phases. Anhydrite, mullite and quartz were still detected, however the intensity of mullite and quartz exhibited little decline with increasing of temperature. When

the temperature rised up to 1000 °C, larnite and grossular disappeared and new crystalline phase, potentially corresponding to anorthite, wollastonite and pseudowollastonite were tracked. The intensity of peaks related to gehlenite and wollastonite improved significantly. The high intensity of gehlenite also appeared in hybrid cement HYC, which means after thermal treatment of 1000 °C, gehlenite formed as main and stable phase in both HYC and HYP cement.

Figure 6.4.6 XRD data of HYP pastes before and after selected treatments.

Fig.6.4.7 shows the diffractograms for the FAN matrix before and after the high-temperature tests. The minority crystalline phases present in the initial fly ash, quartz and mullite were scantily affected by the activation process or exposure to high temperatures. The characteristic halo with 2θ values of 25-35° associated to the formation of an alkaline aluminosilicate gel (N-A-S-H gel) was clearly noted in non-fire FAN matrix. Slightly changes in intensity are observed in this halo when the temperature raised but are difficult to quantify.

Hydroxysodalite was detected in XRD patterns. It formed in the initial FAN matrix as a minority crystalline phase during activation. This phase maintains its stability up to 600 and 800 °C although related peaks were weak at 800 °C. The XRD pattern at 600 °C exhibited similar crystalline components but low intensity, which indicated that exposure at 600 °C lead to poor crystallinity.

After heating to 800 °C, the zeolite was observed start to disappear and nepheline (NaAlSiO_4) to form. Nepheline is kind of feldspar that nucleates at high temperature and closely resembles sodalite in terms of chemical composition, both having a Si/Al ratio of 1.0 (Fernández-Jiménez, Pastor et al. 2010). At 1000 °C, high intensity of presence of albite was detected in addition to nepheline. These transformations involve intermediate sintering and the concomitant formation of a vitreous phase.

Legend:

- C:** Calcite, CaCO_3 , 083-0578;
- H:** Hematite, Fe_2O_3 , 033-0664;
- M:** mullite, 084-1205;
- Q:** quartz, 046-1045,
- S:** Hydroxysodalite, $\text{Na}_8(\text{AlSiO}_4)_6(\text{OH})_2 \cdot 4\text{H}_2\text{O}$, 041-0009;
- N:** nepheline, NaAlSiO_4 , 035-0424;
- al:** albite, ordered, $\text{NaAlSi}_3\text{O}_8$, 009-0466;
- q:** cristobalite, SiO_2 , 039-1425

Figure 6.4.7 XRD data of FAN pastes before and after selected treatments.

6.4.3 ^{27}Al and ^{29}Si MAS NMR study after heat exposure

In last section of XRD patterns study, no significant crystalline difference was observed at 600 °C of selected materials. New crystalline phases have been detected at 800 °C and 1000 °C. In this part, same samples were analyzed by ^{27}Al MAS NMR and ^{29}Si MAS NMR only at 800 °C and 1000 °C.

Fig.6.4.8 exhibited ^{27}Al and ^{29}Si MAS NMR spectra of OPC pastes before and after exposure high temperature (800 and 1000 °C selected). It has been discussed in the former chapter that the signal in ^{27}Al and ^{29}Si MAS NMR spectra its 28 days hydration pastes.

Figure 6.4.8 ^{29}Si MAS NMR spectra of OPC pastes before and after exposure to high temperature (800 and 1000 °C selected).

The ^{29}Si MAS-NMR spectrum for 28 day pastes has been discussed in section 5.4.2.1. The main hydration product C-S-H gel shows the characteristic peaks with resonance of Q^1 and Q^2 . The Q^0 resonance presents the remaining anhydrous cement corresponds to C_3S , C_2S also identified by XRD.

The heated specimen of same pastes revealed evolution of spectra. After heating at 800 °C, the initial C-S-H gel (Q^1 and Q^2 structure) totally decomposed and transformed to Q^0 structure. Peak at -71.6 ppm is related to C_2S , and a small shoulder at -69 ppm and -73.8 ppm appeared as Q^0 structure, then the shoulders disappeared in ^{29}Si MAS-NMR spectrum for samples exposed to 1000 °C. The shoulder at around -69 ppm could be associated with new nesosilicate phase (Q^0) (Alonso and Fernandez 2004) with a structure close to belite (Engelhardt and Michel 1987) or alite (Cong and Kirkpatrick 1996) with less crystalline formation. Two peaks, -71.6 and -73 ppm, were detected in the sample heated at 1000 °C, which related to C_2S and C_3S phases detected in XRD pattern.

^{27}Al MAS NMR spectra of OPC indicated Al transformation with temperature. The spectrum for 28-day hydrated paste exhibited signals associated primarily with the octahedral Al (Al_O) in ettringite and carboaluminates. After heating of high temperature, the signals transferred to 40-to-100 ppm that associated with the presence of the tetrahedral aluminum (Al_T).

Figure 6.4.9 ^{27}Al and ^{29}Si MAS NMR spectra of spectra of HYC pastes before and after exposure high temperature (800 and 1000 °C selected).

Fig.6.4.9 exhibited ^{27}Al and ^{29}Si MAS NMR evolution of spectra for HYC with temperature. According to the former discussion (chapter 5), the main hydration product is a mix of C-S-H, C-(A)-S-H and C-A-S-H gels (Q^1 , Q^2 and Q^3 structure). After 800 °C exposure, signals of ^{29}Si MAS NMR spectrum totally changed. The area related to hydration product of HYC cement disappeared and only exhibited Q^0 structure, which indicated the gels has decomposed as temperature. An intensity peak centred at -71.6 ppm is associated with C_2S . Two shoulders, at -69.8 and -73.9 ppm also were observed. The former peak could be also associated with new nesosilicate phase (Q^0), and the later could be related to unreacted slag content in the paste. An area with very low intensity from -80 to -120 ppm is probably due to unreacted fly ash content come from raw material. From 800 °C to 1000 °C, hybrid cement HYC performed different behaviour to OPC. A series chemical transition happened at this temperature range. From ^{29}Si MAS NMR spectra, the peak related to C_2S (-71.6 ppm) almost disappeared, and new peaks appeared at -74.8(Q^1), -76.3 (Q^1), -83.9(Q^2) and -88.9 (Q^2) ppm. The chemical shift at values of -74.8 and -76.3 ppm can be associated with crystalline phase rankinite ($Ca_3Si_2O_7$) (Hansen, Jakobsen et al. 2003), the intense resonance at -83.9 ppm is related to pseudowollastonite (α - $Ca_3Si_3O_9$) and signal of -88.9 ppm should be generated by wollastonite crystalline phase (β - $Ca_3Si_3O_9$) (Schneider, Cincotto et al. 2001, Hansen, Jakobsen et al. 2003). Generally stable crystalline of wollastonite does, indeed, show three resolved resonance lines at -89.5, -88.9, and -87.8 ppm associated with three different Q^2 site for silicon in the unit cell (Smith, Kirkpatrick et al. 1983, Magi, Lippmaa et al. 1984). Alongside the peak of -88.9 ppm, there were two small peaks observed at -89.9 and -86.9 ppm, which could be related to wollastonite as well. A shoulder centered around -73.2 ppm could be associated to unreacted slag particle. All these phases were detected in XRD pattern in last section. Another main phases confirmed by XRD in this sample is gehlenite. The reference (Smith, Kirkpatrick et al. 1983, Florian, Veron et al. 2012) indicated that gehlenite normally generates a signal at -72.5 ppm in ^{29}Si MAS NMR spectra, but in this work, there is no clearly peak around -72.5 ppm that related to Gehlenite. It could be explained by overlapping of signals in this chemical shift area, such as -73 / -74 ppm normally considered being associated with slag component.

^{27}Al MAS NMR spectra of HYC exhibited similar phenomena of OPC. The spectrum of 28-day hydrated paste has resonance of octahedral Al (Al_O) in ettringite and carboaluminates. After heating of high temperature, the signals disappeared and shifted to the area with presence of the tetrahedral aluminum (Al_T). The ^{27}Al MAS NMR spectra at 800 and 1000 °C exhibited quite similar,

symmetry signal centered around 58 ppm was recorded. This signal could be explained by overlap of several components, unreacted slag, fly ash particle and the tetrahedral Al coordinated in crystalline phase of gehlenite that normally couldn't show resolution due to a significant broadening of lines in tetrahedral Al position (Florian, Veron et al. 2012). However, XRD patterns give clearly result of gehlenite formation, this could be offer evidence to explain ^{27}Al MAS NMR spectra here.

Figure 6.4.10 ^{27}Al and ^{29}Si MAS NMR spectra of HYP pastes before and after exposure high temperature (800 and 1000 °C selected).

^{27}Al and ^{29}Si MAS NMR evolution of spectra for HYP with temperature is illustrated in Fig.6.4.10. The normal paste at 28 days has been analyzed in last chapter by MAS NMR. ^{29}Si MAS NMR spectra of HYP mainly exhibited unreacted fly ash content (Q^4), anhydrous belite clinker (Q^0) and main hydration product: mix of C-S-H, C-(A)-S-H and C-A-S-H gels (Q^1 , Q^2 and/or Q^3).

After heating to 800 °C, ^{29}Si MAS NMR of HYP shows similar trends like OPC and HYC. The signals associated with mix of gels (Q^1 , Q^2 and/or Q^3) disappeared with the decomposing of gels. Peak at -71.5 ppm (Q^0) along with a

shoulder at -72.8 ppm (Q^0) has been recorded. The former resonance is related to C_2S , the later should be related to Q^0 presented in clinker. Unreacted fly ash content also generated a wide, low intensity signal (see HYP-800 spectra).

The spectrum of ^{29}Si MAS NMR of HYP at 1000 °C indicated that recrystallization happened between 800 and 1000 °C. Two groups of new signals associated with Q^1 and Q^2 units appeared. One group is centred at around -74 ppm (Q^1) (-71.5, -72.7, -74.2 and -75.7) and the other group is at around -89 ppm (Q^2) (-84.5, -88.2 and -89.5 ppm). A small shoulder at -71.5 ppm could be related to slightly content of C_2S (larnite) that did not breakdown. Signal at -72.7 ppm is probably associated with gehlenite according to the reference (Smith, Kirkpatrick et al. 1983, Florian, Veron et al. 2012). Previously mentioned in HYC samples, the peaks at -74.2 and -75.7 ppm were generated by rankinite ($Ca_3Si_2O_7$) (Hansen, Jakobsen et al. 2003). The small signal at -84.5 ppm, with the peak at -89.5 ppm together could be associated with crystalline phase anorthite ($CaAl_2Si_2O_8$) (Engelhardt and Michel 1987) combining with XRD results. The existence of resonance at -88.2 ppm possibly associate to wollastonite crystalline phase (β - $Ca_3Si_3O_9$), according to the fact that this phase normally generated three peaks around this chemical shift range, which could be overlapped by other signals generated by anorthite. The signals (Q^4) related to fly ash content did not alter so much and still keep low intensity.

^{27}Al MAS NMR spectra of HYP exhibited a same wide signal centered at around 55 ppm at 800 and 1000 °C. This signal could be explained as overlapping signals generated by tetrahedral aluminum (Al_T) as well. It should contain peaks related to fly ash component, anorthite ($CaAl_2Si_2O_8$) and gehlenite (Baltisberger, Xu et al. 1996, Florian, Veron et al. 2012).

From ^{27}Al and ^{29}Si MAS NMR spectrum evolution, general conclusion could be summarized for two hybrid cements HYC and HYP as following:

- (i) With increasing of exposure temperature up to 800 °C, most octahedral aluminium (Al_O) disappeared and transferred into tetrahedral aluminum (Al_T)
- (ii) The main hydration products: mix of gels, C-S-H, C-(A)-S-H, C-A-S-H and (C, N)-A-S-H in the hardened pastes of 28 days almost decomposed after exposure to 800 °C.
- (iii) The recrystallization process happened between 800 and 1000 °C, C_2S (larnite) start to breakdown at this temperature range and

transferred to group of crystalline phases depending on the chemical composition.

Figure 6.4.11 ^{27}Al and ^{29}Si MAS NMR spectra of FAN pastes before and after exposure high temperature (800 and 1000 °C selected).

Fig.6.4.11 illustrates ^{27}Al and ^{29}Si MAS NMR spectra of FAN pastes with temperature. In last chapter, section 5.2.2.3, it has been discussed that Si^{4+} and Al^{3+} cations are tetrahedrally coordinated and joint by oxygen bonds for FAN 28 day paste. ^{29}Si MAS NMR spectra with distinguish signals are attributed to the presence of silicon tetrahedral surround by zero $\text{Q}^4(0\text{Al})$, one $\text{Q}^4(1\text{Al})$, two $\text{Q}^4(2\text{Al})$, three $\text{Q}^4(3\text{Al})$ and four $\text{Q}^4(4\text{Al})$ aluminum tetrahedral, indicative of an N-S-A-H gel with high silicon content. ^{27}Al MAS NMR spectra exhibited a narrow signal at 58 ppm, which illustrated Al is always surrounded with four silica groups.

After thermal treatment (at 800 and 1000 °C), the ^{27}Al and ^{29}Si MAS NMR spectra represented a obvious change. The shift of resonance after thermal treatment reflected certain chemical transformations taking place in the matrix.

The post treatment (to 800 and 1000 °C) ^{29}Si spectrum for FAN shows a very wide asymmetric signal centred at -95 ppm. It could be associated with new formation of phases and gel unaffected by the thermal treatment (Fernández-Jiménez, Vallepu et al. 2006). The narrow peak at 58 ppm of ^{27}Al spectra for FAN-28 day sample changed towards to a wide resonance around + 55 ppm. The shifted observed may be due to the overlap with Al_T in the new phase and the gel, which did not all transform to new phases.

6.4.4 Microscopy study of materials after exposure to high temperatures

The analysis of the microstructure of material has been discussed in this section. Fig.6.4.12 to 6.4.17 illustrated the SEM micrographs of selected pastes after high temperature exposure (800 and 1000 °C) and EDX analysis of selected points.

In Fig.6.4.12a and b, when temperature reaches 800 °C, the cement structure contained more pores and has no consistency. EDX analysis exhibited high CaO/SiO_2 (Point 1, the value $\text{CaO} / \text{SiO}_2$ is 3.36) points of matrix. This could be due to simultaneously exist of $\text{C}_2\text{S} / \text{C}_3\text{S}$ and lime (CaO , see point 2) in the matrix. After heating to 1000 °C, the pastes lost strength and become into small particle. SEM images were graphed as conducted on powders. The matrix has no consistency and seemed become totally granular in morphologically. EDX analysis exhibited the various phases in presence (most of points) tend to be uniform with the value of $\text{CaO} / \text{SiO}_2$ between 2 and 3 (point 3, $\text{CaO} / \text{SiO}_2 = 2.7$) and point associated with CaO (Point 4). In XRD pattern, larnite and lime have been confirmed to be main crystalline phases in the paste after 1000 °C exposure.

Figure 6.4.12 Backscattered SEM micrographs of OPC paste after high temperature exposure and EDX analysis of selected points. (a)-(b) 800 °C, (c)-(d) 1000 °C. Note: At 1000 °C, SEM image of OPC is for powder..

SEM micrographs of HYC matrix exposed to 800 and 1000 °C were illustrated in Fig. 6.4.13. The general scanning (Fig.6.4.13a and Fig.4.2.13d) for pastes

heated at 800 and 1000 °C have not showed distinguish morphologically. The cement structure performs a lack of binder (gels) property. This matrix characteristic suggested a visible decrease of the material resistance.

Figure 6.4.13 Backscattered SEM micrographs of HYC paste after high temperature exposure. (a)-(c): At 800 °C, (d)-(f): At 1000 °C.

In Fig.6.4.13a to 6.4.12c, after heated up to 800 °C, some large particle (particle1, and particle 2) were observed in the matrix embedded inside other tiny granular particles with high Ca and Si content, which could be clinker or slag particle. A crystalline phase which attributed to CaSO_4 was detected and confirmed by EDX analysis (See Fig.6.3.13, Point 3). Between the large particles, the structure

exhibited consistency (Point 4) with similar element component of gels that precipitated in HYC.

Table 6.4.1 EDX analysis of selected point in Fig.6.4.12f.

Points	Normalized element composition by mass (%)								Radio (by molar)	
	O	Na	Mg	Al	Si	S	Ca	Fe	Ca/Si	Al/Si
a	39.14	0.70	0.55	7.91	12.85	1.13	34.28	3.41	1.87	0.64
b	38.76	0.82	0.67	5.75	15.22	0.00	35.63	3.13	1.64	0.39
b	38.87	0.91	0.53	2.78	15.95	1.06	38.49	1.38	1.69	0.18
d	39.00	1.01	0.99	7.99	12.77	0.87	33.31	4.05	1.83	0.65
e	39.69	0.81	1.06	10.48	13.52	0.21	32.91	1.04	1.70	0.80
f	38.89	1.25	1.26	7.33	14.01	0.20	33.29	3.23	1.66	0.54

Figure 6.4.14 EDX analysis of selected points in Figure 6.4.12.

When temperature reaches 1000 °C, the structure of pastes exhibited totally granular and tiny. Crystalline-like phases were observed in the matrix (see Fig.6.4.13c and 6.4.13d). Selected points (point 5 and 6) presented EDX analysis. Combining with XRD results, it could be associated with new gehlenite phase. In Fig.6.4.13d, it exhibited clearly coral-like structure with an average Ca/Si ratios around 1.7 (see Table 6.4.1) and various Al/Si ratios (< 1) obtained as well.

Although identified crystalline phases which detected by XRD have been not observed morphologically in SEM images. It also indicated that the gel structure of paste broke down with temperature into granular structure by SEM information. At 1000 °C, this structure exhibited crystalline-like property.

Figure 6.4.15 Backscattered SEM micrographs of HYP paste after high temperature exposure. (a)-(c): At 800 °C, (d)-(f): At 1000 °C.

Fig.6.4.15 exhibited SEM micrographs of HYP when it exposed to high temperature. It is observed similar morphological in general images for the matrix at 800 and 1000 °C. Unreacted fly ashes have been marked in Fig.6.4.15a

and 6.4.15d. They come from the raw materials with different sizes. A numbers of pores between particles were founded distributed in the matrix (dark zone) that made materials lose mechanical strength.

After heating to 800 °C, the matrix structure evolved from pasty to granular where the binder (gel) seems to have disappeared. Between the fly ashes, the structure exhibited no consistency (see Fig.6.4.15b and 6.4.15c). The EDX analysis showed various Ca/Si ratios with high Al content (Point 1 and Point 2), which is similar to the gel.

The images of 1000 °C presented crystalline-like structure. The matrix becomes totally granular along with fly ash content. EDX analysis of select point is showed in Fig.6.4.16. Different composition of elements, mainly in aluminum, calcium and silicon could be related to new crystalline phased which detected in XRD. However, it is not exactly sure of this.

Figure 6.4.16 EDX analysis of selected points in Figure 6.4.14.

SEM images indicated that after exposure to 800 °C and 1000 °C, the cement paste HYP morphologically changed to different structure when comparing with the normal pasted SEM (in section 5.4). The main hydration product of mix gels

totally decomposed with high temperature. New phases with tiny and crystalline-like structure were obtained.

SEM observations of FAN paste after high temperature exposure (800 and 1000 °C) are shown in Fig.6.4.17. Fig.6.4.17a and 6.4.17c exhibit general scanning image of matrixes; Fig.6.4.17b and 6.4.17d show details of microstructure. The finding was summarized as following:

Obvious morphological distinguishes were observed, at 800 °C, unreacted various size fly ash particle and aluminosilicate gel (N-A-S-H gel, see point 2 EDX analysis) more or less homogeneous distributed in the matrix. The microstructure performed more compact and better inter-particle bonding (see Fig.6.4.17(c)) due to sintering and viscous flow of aluminosilicates during heating (Rickard, Temuujin et al. 2012) which could explained its best compressive strength (nearly 40 MPa, see section 6.4.3) after 800 °C exposure. At 1000 °C, in contrast, the matrix containing unreacted fly ash particle presented at 800 °C transformed to a matrix with large pores generated by vitreous bonds framework. This structure could perform good compressive strength and bending strength after thermal treatment (see Fig.6.3.7 and 6.3.8) due to the high mechanical property of vitreous bonds, although it contained lot of huge pores.

New crystalline phases detected in XRD, nepheline (at 800 and 1000 °C) and albite (at 1000 °C), were not morphologically found in SEM images. The reason could be at 800 °C, nepheline is lower crystallinity (low intensity of corresponding peaks in Fig.6.4.6) and at 1000 °C, even though XRD exhibited high intensity of new two crystalline phases, they were probably wrapped around by melting vitreous phases, and were not visible to observed by SEM. EDX analysis could be assigned to N-A-S-H gel at 800 °C, and calcium, iron, and potassium were also detected came from raw materials. At 1000 °C, similar composition of N-A-S-H gel was obtained by EDX for vitreous bonds, which indicate that this vitreous probably come from melting phases of raw fly ash particle and/or amorphous aluminosilicate gels.

Figure 6.4.17 Backscattered SEM micrographs of FAN paste after high temperature exposure and EDX analysis of selected points. (a)-(b) 800 °C, (c)-(d) 1000 °C. F: fly ash particle; P: pores; V: Vitreous bond.

6.4.5 DTA and TG investigation

DTA/TG are available techniques aimed to reveal through measurement of mass loss or differential temperature evolution the major phenomena taking place in the material such as hydration or chemical phases appearance or disappearance (Djaknoun, Ouedraogo et al. 2012). Some investigation based on thermal analysis, particularly on OPC, have been made by different researchers (Piasta, Sawicz et al. 1984, Alonso and Fernandez 2004, Stepkowska, Blanes et al. 2004, Mendes, Sanjayan et al. 2007, Djaknoun, Ouedraogo et al. 2012). The main changes happening in cement pastes with temperature are summarized as following according to the reference:

- (i) Up to 400 °C: In this temperature range, water transportation mainly happened, including free water (up to 100 °C), hydrate water (up to 220 °C), and C-S-H gel water (up to 400 °C).
- (ii) From 400 to 600 °C: Dehydration of calcium hydroxide. The chemical reaction here is described: $Ca(OH)_2 \leftrightarrow CaO + H_2O^{gas}$.
- (iii) From 600 to 800 °C: Decarbonation of calcite. The chemical reaction here is described: $CaCO_3 \leftrightarrow CaO + CO_2^{gas}$.

Two chemical process, liberation of water from the decomposition of $Ca(OH)_2$ and liberation of CO_2 , can caused a rapid increase in total porosity of matrix (Piasta 1984), which very agreed with the results in MIP test (see Fig.6.4.1).

The 28 day pastes samples of material (see Table 6.1.1) were prepared and conducted on thermogravimetry test. The thermal analyses are presented in Fig.6.4.17 (DTA) and 6.4.18 (TG). Peak information for DTA curves and the mass loss of TG analysis were listed in Table 6.4.2 and Table 6.4.3 with temperature.

Figure 6.4.18 DTA curves for the paste of 28 testing age of materials.

Figure 6.4.19 TG curves for the paste of 28 testing age of materials.

Table 6.4.2 Peak / shoulder information of DTA curves.

Paste	Temperature (°C)				
	Shoulder	Peak	Shoulder	Peak	Peak
OPC	around 50	96.89	around 150	436.11	655.93/691.30
HYC	around 50	91.05	around 140	357.36/436.41	672.77
HYP	around 50	93.79	around 160	/	680.54
FAN	around 50	104.66	/	/	614.41

Table 6.4.3 Weight losses of material in TG tests.

Paste	Weight losses versus temperature (%)				
	25-200 °C	200-400 °C	400-600 °C	600-800 °C	800-1000 °C
OPC	8.05	2.98	3.41	3.71	0.78
HYC	6.76	2.26	2.55	3.42	0.20
HYP	7.07	1.99	3.49	2.67	0.22
FAN	3.65	1.39	0.84	0.65	0.78

In all four cements a series of endothermic (overlap) peaks appears between room temperature and 200 °C (see Fig.6.4.18 and Table.6.4.2). These peaks are partly associated with the loss of water. In OPC, HYC and HYP samples, the first loss of mass corresponds to the drying of the pastes (free water), decomposition of ettringite (hydrate water, which were confirmed by XRD results in section 5.4.1) and dehydration of gels (gel water). For FAN paste, the loss of weight mainly due to free water escape and dehydration of gels.

These peaks give rise to weight losses of 8.05% for OPC and of weight losses on the order of 6.76% and 7.07 % for HYC and HYP respectively. This may be due to the loss of water in reaction products (which in the case of ettringite) or the fact that the water content in the gels formed in hybrid cements is lower. FAN alkali cement display an even lower signal with a clearly inferior weight loss (3.65%). The interpretations are similar to those applied to the case above: a lower degree of reaction or formation of gels whose water content is lower.

From 200 to 400 °C, weight loss continued (see TG curves), and in DTA curves it performed similar in OPC, HYC and HYP with a period of stable line. The mass losses corresponds to gels dehydration (Djaknoun, Ouedraogo et al. 2012). FAN curves showed a slightly decline in DTA curves without peaks, its loss of weight could be explained also by dehydration of gels.

While it is true that the quantity of water present in C-A-S-H and N-A-S-H gels has not yet been quantified, based on the fact that the structure of C-A-S-H gels is two dimensional and that of N-A-S-H gels is three dimensional, it logically follows that when the number of bonds increases in the gels (polymerization by condensation), the water content of the gels declines. Therefore, it should be believed that these water loss reductions are probably due to some extent to the lower degree of reaction of the cement but primarily to the lower water content of the more highly polymerized gels.

As the temperature continues rising, another endothermal peak appears at around 436° for OPC and HYC (see Table 6.4.2). This peak is associated with the breakdown of the portlandite (summary (ii)). This signal is much more intense (DTA curves) in OPC than in HYC with more weight loss in TG curves (Green marked). There is no small peak in this area related to portlandite of HYP (in Fig.6.4.18). It means that there is no portlandite in HYP pastes. In Fig.6.4.19, around 436 °C, obvious weight loss was not achieved, which confirms it; this result was also agreed with XRD data for HYP paste in section 5.4.1.

The endothermal peaks at temperatures of between 600 to 800 °C, which appear in OPC, HYC and HYP, are associated with the release of CO₂ from the calcium carbonates (summary (iii)). The results are also supported by XRD data in section 6.4.2. It is clearly shown that the peaks related to calcite at 600 °C XRD patterns for OPC, HYC and HYP disappeared in the patterns of sample exposed at 800 °C.

The FAN cements present none of the signals discussed above. It displays only an endothermal shoulder centred at 614 °C with very minor mass variations. This indicates that transformation reactions could be taking place (possibly amorphization followed by recrystallization) at this temperature range (Fernández-Jiménez, Palomo et al. 2008).

6.5 Discussion

The term fire resistance is frequently used to assess the behaviour after firing of different samples. It normally is also defined as different criteria such as linear and volume changes, stability of strength etc. In this part of work, the samples were investigated for mechanical and physicochemical behaviours at high temperature.

Four different materials (OPC, HYC, HYP and FAN) were utilised in this study. The original chemical composition, especially $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, attribute to different high temperature behaviour of selected materials. Two trials were conducted on samples to track their mechanical behaviour at high temperature, here described “in situ” and “post”. In Trial 1 (in situ), materials were loaded to failure at high temperature, in Trial 2 (post) they were subjected to thermal shock between the target and ambient temperature. According to the results in experiments, discussion could be proposed by different temperature range.

❖ Under 400 °C exposure

At temperature range until 400 °C, OPC, HYC and HYP performed similar quasi-elastic behaviour (in situ), the mechanical strength (both Trail 1 and Trial 2) decreased with temperature increasing dynamic elastic modulus declined as well. The reason could be related to water liberating during exposure to heat and until 400 °C affects the mechanical behaviour. This water partially comes from free water, hydrates water and gel water which discussed before in TG / DTA study. Water steam (above 100 °C) and the entrained air creates a high pressure in cement pastes practically generate positive pressure on the internal walls of the microspores. It caused an overall decline in cement paste strength due to the appearance of cracks in the matrix.

C. Alonso et al ([Alonso and Fernandez 2004](#)) studied ^{29}Si MAS NMR spectra of OPC pastes from 100 to 750 °C, it clearly showed an evolution of signals which related to C-S-H gel dehydration process: Q^1 and Q^2 silicon site shift to Q^0 site. The dehydration of gels as well contributed to materials deterioration, according to the fact that the gels are primarily responsible for the mechanical properties of cementitious materials ([Neville 1995](#), [H.F.W.Taylor 1997](#)). Hybrid cement HYC and HYP performed more resistance probably due to less water content in the matrix.

Alkali-activated cement binder FAN exhibited opposite behaviour. This material also lose water (DTA / TG results), part of this water may come from zeolite combined water, which has no effect on the dimensional stability of materials. The matrix of FAN own large number of pores, especially larger than 0.2 μm (see Fig.6.4.3). These pores could facilitate the escape of moisture when heated, thus causing minimal damage to this materials.

❖ *From 400 to 600 °C exposure*

The dehydration of portlandite ($\text{Ca}(\text{OH})_2$) happened in this temperature range. It decomposed into calcium oxide and water (gaseous form). It has reported (Alarcon-Ruiz, Platret et al. 2005) the dehydration process happened together with rapidly rehydration after hydration. Moreover, the calcium oxide formed is a very hygroscopic compound whose volume increase as it rehydrates. The pressure generated by liberated water and rehydration of calcium (volume increase) could reduce the compressive strength of materials further may cause structural collapse.

Above 400 °C, OPC samples presented a considerable decrease in compressive strength and could not be tested of TPB in-situ condition at 600 °C. Severe crack were obtained in SEM of 400 °C sample in fracture surface, which also confirmed the beginning of deterioration of OPC. HYC and HYP exhibited more resistance in mechanical behaviour especially in in-situ bending test (they were allowed to be tested with same condition). It could be explained by less content of $\text{Ca}(\text{OH})_2$ in hydrate pastes of HYC and HYP. The reason of low $\text{Ca}(\text{OH})_2$ content in hybrid cement are: i) less C_3S content in raw cement material lead to less reaction product of portlandite; ii) the pozzolanic reaction happened in this matrix; iii) $\text{Ca}(\text{OH})_2$ reacted with Na_2SO_4 , generating more alkalis in the system. The higher alkaline content raised the pH of the pore solution, favouring SCMs dissolution and the possible precipitation of alkaline reaction products (N-(C)-A-S-H-like gels. HYP 28-day paste has no portlandite content (confirmed by XRD and TG/DTA) could be related to consumption of it in pozzolanic reaction with fly ash content.

Another data from pore structure analysis by MIP could also explain mechanical behaviour between OPC and two hybrids cement (see Fig. 6.4.3). After exhibited 600 °C, the percentage of pores with diameters greater than 0.05 μm increased but less in HYC and OPC pastes, may be caused by the formation of macro cracks.

FAN paste performed different behaviour. In trial 1 (in situ), the compressive strength increased dramatically from 400 to 600 °C. However in trial 2 (post), the strength showed slightly decline. The phenomena could be explained combing the reference and experiments.

At 600 °C, from in-situ compressive stress-strain curve, only linear curve with failure was obtained. It cannot be described as elastic behaviour due to very large deformation. From in-situ three point bending stress-strain curve, large

permanent deformation was recorded. When FAN was exposed to 600 °C, partial of melting occurs but not soften. When compressive test started, under the load, partial melting phase could lead to the sealing of cracks and pores, which make the matrix more compact and performed high compressive strength in situ and post thermal treatment.

❖ From 600 to 800 °C exposure

In this temperature range, several chemical transformation happened in OPC and hybrid cement. Including decarbonation of calcite (discussed in section 6.4.5); totally dehydration / decomposed of gels which confirmed by ^{29}Si MAS NMR study. The Q^1 , Q^2 and Q^3 silicon site was obtained to transfer to Q^0 site. Both two processes contributed to the collapse of cementitious materials of mechanical property. SEM graphs showed little

FAN paste totally soften in this temperature range, which confirmed by in-situ test (both compressive and bending). The same result was also recorded in former research by the same group. ^{27}Al and ^{29}Si MAS NMR and XRD founding confirmed recrystallization happening. The high compressive strength in trial 2 (post) indicated that solidification after cooling occurred followed sintering. Nepheline was detected as new phase in FAN pastes. The presence of alkalis and high aluminium content makes these feldspathoidal-like phases stabilize (Bakharev 2006).

❖ From 800 to 1000 °C exposure

From 800 to 1000 °C the main recrystallization happened to phase. Fig.6.5.1 and 6.5.2 illustrated crystalline phase's changes between 800 °C to 1000 °C.

Different to OPC pastes, after high temperature exposure (>800 °C), hybrid cement exhibited a group of new crystalline phases: rankinite, wollastonite, pesuowollastonite (without Al) and gehlenite and anorthite (only HYP) with Al rather than lime and larnite for OPC. The presence of alkalis in the medium also favors recrystallization of the new phases at high temperatures. It makes hybrid cement (HYC and HYP) not collapse inside water (see section 6.3.1). From the illustration, other trends could be described that with temperature increase, the crystalline phase tends to high $\text{SiO}_2\text{-Al}_2\text{O}_3$ direction.

Figure 6.5.1 Illustration of the location of four cement paste on ternary diagrams for $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$. The crystalline phases implied by XRD data at 800 °C exposure.

Figure 6.5.2 Illustration of the location of four cement paste on ternary diagrams for $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$. The crystalline phases implied by XRD data at 1000 °C exposure.

The differences in mechanical strength behaviour in the materials depending on the type of trial can be attributed to the different test conditions. Whereas in “*In-situ test*”, the materials were loaded to failure at high temperatures to stabilize the specimen at the test temperature to prevent preloading deterioration due to steep temperature gradients, in “*post-thermal test*” they were subjected to

thermal shock between the target and ambient temperatures, but no load was applied during thermal treatment.

In Trial 1 (*In-situ test*), then, the appearance of new phases at high temperatures occasioned local flaws and therefore the gradual deterioration of mechanical strength and toughness with increasing temperatures, especially in OPC. The presence of alkalis in hybrid cements and especially in FAN binders are responsible of the appearance at high temperatures of molten or viscous phases in the matrix gave rise to local plastic deformation and consequently the opposite effect. In this case, the viscous phases can enhance compressive strength by sealing and closing cracks. This effect is very relevant in FAN binder, where these phases became increasingly fluid with rising temperatures and lost this capacity, mechanical strength declined.

Moreover, the steep heating and cooling rates in the "post-thermal treatment" generated new or intensified the existing flaws and cracks, for the material was unable to absorb the thermal strain generated, ultimately leading to local failure. Decay due to the increase in the size of critical flaws was particularly obvious in the Trial 2 bending tests and in OPC. However, in FAN binder, the presence of molten phases became more fluid and, with sufficient time and sufficiently high temperatures, they were able to repair the flaws and cracks present in the material. Because the new microstructure in the closed or narrowed cracks persisted when the material cooled, the strength tests conducted at ambient temperature yielded higher values than in OPC. This effect was particularly clear in the compression tests following Trial 2 (Figure 6.3.5). Hybrid cements show and intermediate behaviour between OPC alkali cement (FAN)

Finally, while the fracture toughness values obtained were low in all cases, as expected, the hybrid cement (HYC) and FAN binder performed better in this respect than the Portland cement samples. This very interesting finding opens up new possibilities for developing inexpensive cements that are much tougher than traditional OPCs.

6.6 Concluding remarks

Cements based on Portland cement present a drastic drop in mechanical strength as of a point between 400 °C and 600 °C, due to water loss in the C-S-H gel and the breakdown of the gel. Until 800 °C, the gel totally decomposed. This process is observed in both types of tests, in both in situ and post mechanical tests. In other words, once the material has cooled, it does not recover even a small extent of its initial mechanical strength. The temperature causes the formation of CaO, which could be rehydrated in contact with water.

Fly ash-based alkali cements maintain and even increase their mechanical strength up to 600°C. Their high alkali content favours the formation of a molten phase at temperatures of around 600 to 700 °C. The solidification of this phase gives rise to the formation of nepheline-type crystalline phases that improve mechanical strength under compressive stress after cooling but do not improve mechanical strength under flexural stress, due to dimensional stability problems.

Hybrid cements, HYC, and HYP, present a behaviour that is somewhere between that of OPC and that of fly ash-based alkali cement. Hybrid cements have better behaviour than OPC at high temperature, especially after 600 °C, and they are stable when cooling in water after high temperature treatment. On the other hand, hybrid cements did not molten like FAN under loading during in situ test, although they have lower strength than FAN in post-thermal tests. Their superior behaviour is associated with the fact that hybrid cements have lower calcium content than OPC.

Between two hybrids cements, HYC performed better high temperature behaviour than HYP. HYC has higher both in situ mechanical strength and residual strength after high temperature exposure.

7 Conclusion and future work

7.1 Conclusions

Throughout this work the effect of temperature on some specific cementitious binder materials was widely investigated. These materials were produced industrially with lower clinker content and higher supplementary materials content for its use in future as alternative eco-friendly binder materials.

Based on the experimental studies and according to the objective that proposed in chapter 2, the conclusions of this thesis can be summarized as following.

➤ **Effect of temperature on the early hydration (in pre-curing process) of binder materials.**

1. At ambient temperature (pre-cured at 25 °C), industrial hybrid cement (HYC and HYP) with a low clinker content set and hardened when hydrated with water, giving rise to a binder with acceptable mechanical strength.
2. Unlike OPC and FAN, hybrid cement owes its good mechanical strength to the main hydration product, a mix of cementitious gels: C-(A)-S-H, C-A-S-H, and (N, C)-A-S-H (detected in HYP). The complex of participation of hydrate products due to the content of supplementary materials.
3. Higher pre-curing temperature (85 °C) expedites hydration reaction for hybrid cements in much the same way as in OPC and alkaline cements. The initial reaction was accelerated by raising temperature, which enhanced dramatically 3-day mechanical strength. However, the subsequent development of mechanical strength was slower than when the cement was pre-cured at ambient temperature.
4. Solid activator that initially added in hybrid cement production (NaSO_4 dominant) could offer alkalinity environment when they hydrated. It offers the possibility to use solid activator in the industry hybrid cement production for improving their performance.

➤ **Effect of high temperature on the hardened pastes.**

1. With the temperature rising up to 600 °C, hybrids cements, HYC and HYP decline in mechanical strength fracture toughness, and modulus of elasticity (in situ) similar to OPC. Between 400 to 600 °C, OPC lost strength, however hybrids cement performed better behaviour (in situ and post-thermal

treatment) than OPC. Brittle failure is observed in all cases. HYC performed better high temperature behaviour than HYP in both two trials.

2. Water transportation, dehydration of Ca(OH)_2 , decarbonation of calcite and decomposition of hydrated gels contributed to the mechanical strength loss of OPC, and hybrids cements HYC and HYP at high temperature.
3. Alkali-Fly ash cement: the formation of a molten phase is at temperature of around 600 to 700 °C. The pseudo-plastic strain taking place in FAN over 600 °C. The recrystallization and solidification of molten phase gives improve mechanical strength under compressive stress after cooling.
4. Their better behaviour of hybrids cements at temperature of over 800 °C is associated with the fact that hybrids cements have lower calcium content and therefore give rise to gehlenite- and rankinite-type poorly hydraulic phases rather than larnite and lime.
5. After 800 °C exposure, hybrids cements and alkali-Fly ash cement maintain stable when cooled directly with water. OPC lost strength and decomposed quickly in water.

7.2 The future work

There are several possible research lines in order to continue the present study:

1. The concrete made from hybrid cement should be investigated, including the mechanical strength and fire resistance
2. More study in hybrid cement is needed to determine heat conduction through a sample when exposed to the standard fire defined by ISO 834, as well as the relation between the thermal resistance of the protection layer and the thickness of an equivalent concrete protection.
3. With large size concrete specimen, the fracture toughness and fracture energy could be an interesting research line to continue for understanding their future behaviour.
4. For alkali-fly ash cement, the type of activator used could influence the high temperature behaviour, the effect of different cations (K^+ , Na^+ etc.) and the Na/Si (Al) ratio is worthy to be studied.
5. Hybrid cement could be used as alternative binder materials. The manufacture of this cement with different composition (Clinker + SCMs + solid activator) also should be continued for improving its propert.

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