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“Processing and characterisation of calcium sulphoaluminate (CSA) eco-cements with tailored performances”

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Processing and characterisation of calcium sulphoaluminate (CSA) eco-cements with tailored performances

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Que la presente memoria realizada por Dª Marta García Maté, titulada: "Processing and characterisation of calcium sulphoaluminate (CSA) eco-cements with tailored performances", ha sido realizada bajo nuestra dirección en el Departamento de Química Inorgánica, Cristalografía y Mineralogía de la Facultad de Ciencias de la Universidad de Málaga. Este trabajo reúne contenido científico suficiente y las condiciones necesarias para ser presentado y defendido ante el tribunal correspondiente para optar al Grado de Doctora.

Málaga a 22 de Octubre de 2014

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A mi madre y mi padre

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Nomenclature

In order to simplify the writing and presentation of chemical formulations, cement nomenclature will be used hereafter:

C = CaO

S = SiO_2

A = Al_2O_3

F = Fe_2O_3

K = K_2O

N = N_2O

$\underline{S}$ = SO_3

M = MgO

B = B_2O_3

H = H_2O

$\underline{C}$ = CO_2

P = P_2O_5

T = TiO_2

The compounds are written as follows:

- $Ca_4Al_6SO_{16}$ = $4CaO \cdot 3Al_2O_3 \cdot SO_3$ = $\mathbf{C_4A_3\underline{S}}$ = ye'elimite
- Ca_2SiO_4 = $2CaO \cdot SiO_2$ = $\mathbf{C_2S}$ = belite
- Ca_3SiO_4 = $3CaO \cdot SiO_2$ = $\mathbf{C_3S}$ = alite
- $Ca_4Al_2Fe_2O_{10}$ = $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$ = $\mathbf{C_4AF}$ = tetracalcium aluminoferrite
- $Ca_3Al_2O_6$ = $3CaO \cdot Al_2O_3$ = $\mathbf{C_3A}$ = tricalcium aluminate
- $CaTiO_3$ = $CaO \cdot TiO_2$ = $\mathbf{CT}$ = perovskite
- $Ca_2Mg(Si_2O_7)$ = $2CaO \cdot MgO \cdot 2SiO_2$ = $\mathbf{C_2MS_2}$ = akermanite
- $CaSO_4 \cdot 2H_2O$ = $CaO \cdot SO_3 \cdot 2H_2O$ = $\mathbf{C\underline{S}H_2}$ = gypsum
- $CaSO_4 \cdot 0.5H_2O$ = $CaO \cdot SO_3 \cdot 0.5H_2O$ = $\mathbf{C\underline{S}H_{0.5}}$ = bassanite
- $CaSO_4$ = $CaO \cdot SO_3$ = $\mathbf{C\underline{S}}$ = anhydrite
- $Ca_2Al_2SiO_7$ = $2CaO \cdot Al_2O_3 \cdot SiO_2$ = $\mathbf{C_2AS}$ = gehlenite
- $CaAl_2O_4$ = $CaO \cdot Al_2O_3$ = $\mathbf{CA}$ = calcium aluminate

- $Ca_{12}Al_{14}O_{33} = 12CaO \cdot 7Al_2O_3 = \mathbf{C_{12}A_7}$ = mayenite
- $Ca_5(SiO_4)_2(SO_4) = 5CaO \cdot 2SiO_2 \cdot SO_3 = \mathbf{C_5S_2\underline{S}}$ = ternesite
- $CaCO_3 = CaO \cdot CO_2 = \mathbf{C\underline{C}}$ = calcite or vaterite
- $Ca_6Al_2(OH)_{12}(SO_4)_3 \cdot 26H_2O = 6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O = \mathbf{C_6A\underline{S}_3H_{32}}$ = ettringite (AFt)
- $2Ca_2Al(OH)_6(SO_4)_{0.5} \cdot 3H_2O = 4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O = \mathbf{C_4A\underline{S}H_{12}}$ = monosulphate (AFm)
- $Ca_2Al(OH)_6[AlSiO_2(OH)_4 \cdot 3H_2O] = 2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O = \mathbf{C_2ASH_8}$ = stratlingite
- $Ca_2Al(OH)_6[Al(OH)_4 \cdot 3H_2O] = 2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O = \mathbf{C_2AH_8}$ = dicalcium aluminate hydrate
- $Ca_3Al_2(OH)_{12} = 3CaO \cdot Al_2O_3 \cdot 6H_2O = \mathbf{C_3AH_6}$ = hidrogarnet
- $Ca_3Al_2(SiO_4)_3 = 3CaO \cdot Al_2O_3 \cdot 3SiO_2 = \mathbf{C_3AS_3}$ = garnet
- $Ca_3(Al_{0.5}Fe_{0.5})_2(SiO_4)(OH)_8 = 3CaO \cdot 0.5Al_2O_3 \cdot 0.5Fe_2O_3 \cdot SiO_2 \cdot 4H_2O = \mathbf{C_3Al_{0.5}Fe_{0.5}SH_4}$ = iron-hidrogarnet
- $2Al(OH)_3 = Al_2O_3 \cdot 3H_2O = \mathbf{AH_3}$ = gibbsite
- $Ca(OH)_2 = CaO \cdot 2H_2O = \mathbf{CH}$ = portlandite
- $2Fe(OH)_3 = Fe_2O_3 \cdot 3H_2O = \mathbf{FH_3}$ = ferric hydroxide
- $SiO_2 = \mathbf{S}$ = quarzt
- $CaO = \mathbf{C}$ = lime
- $MgO = \mathbf{M}$ = periclase

Also have been used occasionally abbreviated names or initials to refer to some terms. Thus, for example:

- OPC: Ordinary Portland Cement
- CSA: Calcium Sulpho-Aluminate
- BCSA: Belite Calcium Sulpho-Aluminate

- aBCSA: active Belite Calcium Sulpho-Aluminate
- BCSAF: Iron-rich Belite Calcium Sulpho-Aluminate
- BCSAA: Aluminum-rich Belite Calcium Sulpho-Aluminate
- ACSA: Alite Calcium Sulpho-Aluminate
- CAC: Calcium Aluminate Cement
- SCMs: Supplementary Cementitious Materials
- FA: Fly Ash
- BFS: Blast Furnace Slag
- SF: Silica Fume
- LS: LimeStone
- HLR: High Lignin Residue
- HLRA: High Lignin Residue Ash
- LXRPD: Laboratory X-Ray Powder Diffraction
- SXRPD: Synchrotron X-Ray Powder Diffraction
- HT-SXRPD: High-Temperature Synchrotron X-Ray Powder Diffraction
- RQPA: Rietveld Quantitative Phase Analysis
- XRF: X-Ray Fluorescence
- DTA-TG: Differential Thermal Analysis-ThermoGravimetric
- MIP: Mercury Intrusion Porosimetry
- SEM: Scanning Electron Microscopy
- LoI: Loss of Ignition
- ACn: Amorphous and Crystalline non-quantified
- w/c: water to cement ratio
- w/b: water to binder ratio
- ICSD: Inorganic Crystal Structure Database
- SRM: Standard Reference Material
- RECCE: Reducing Energy Consumption and CO_2 Emission

- IUPAC: International Union of Pure and Applied Chemistry
- ETA: European Technical Approval
- DIBt: Deutsches Institut für Bautechnik
- EPS: Expanded Polystyrene
- PTFE: Polytetrafluoroethylene

- a#x: article number x
- c#x: article in collaboration number x

Abstract

Abstract

Climate change mitigation usually involves the reduction of greenhouse gases emissions, in general, and carbon dioxide (CO_2) in particular. Every tonne of Ordinary Portland Cement (OPC) produces about one tonne of carbon dioxide. Consequently, OPC production accounts for 5-6% of anthropogenic carbon dioxide emissions and for 4% of total global warming.

Due to these environmental problems the industry of building materials is under increasing pressure to reduce the energy used in production of Portland cement clinker and the associated greenhouse gas emissions. Moreover, Portland cement is not the ideal binder for all construction applications, as it suffers durability problems in particularly aggressive environments. Hence, there is a growing interest in the development, characterization, and implementation of alternatives to Portland cement as a binder in concrete. One of the most interesting alternatives is calcium sulphoaluminate cements (CSA).

CSA cements are considered environmentally friendly materials because their manufacture process releases less CO_2 into atmosphere than OPC, due to this they are labelled as eco-cements. The carbon dioxide emissions can be classified in two main categories: those coming from raw materials and those from the operation processes (millings, kiln operation, and so on). Raw materials and products obtained during the clinkering process are well known. For example, the production of one ton of OPC clinker composed of 65 wt% of C_3S, 15 wt% of C_2S, 10 wt% of C_3A and 10 wt% of C_4AF released 0.54 tons of carbon dioxide. However one ton of CSA clinker composed by 65 wt% of $C_4A_3\underline{S}$, 20 wt% of C_2S, 9 wt% of $C\underline{S}$ and 6 wt% C_4AF releases 0.27 tons of CO_2. Consequently, a reduction in carbon dioxide emissions by 49% due to decomposition of raw material can be attained.

Moreover, cement production is a process of high energy demand, so it is important to consider emissions from fuel consumption to achieve high clinkering temperatures in the kiln and thus quantify CO_2 emissions. However, this is not an easy task as it is directly related to the type of processing equipment and the specific chosen fuel. Several studies estimate an emission of ~0.28-0.34 t of CO_2 per ton of clinker produced due to the burning of coal in the kiln. The reduction in CO_2 emissions coming from the burning of the fuel can be achieved by different strategies including the reduction of clinkering temperature. This is the case of CSA clinker production where the operating temperature can be reduced down to ~1250ºC, ~200ºC lower than that of OPC production, with a concomitant reduction of up to 0.04 t of CO_2 per ton of CSA clinker produced. CO_2 emissions derived from electricity consumption for grinding in OPC clinker production are not negligible. In fact, 0.09 t of CO_2 per ton of clinker produced are calculated, assuming that fossil fuels are used to produce the electricity. Since the lower firing temperatures lead to a CSA clinker which is generally easier to be ground, hence energy savings also occur in the grinding of CSA clinker compared to OPC. Therefore, reduction on the electricity consumption yields a depletion of up to 0.02 t of CO_2 emissions. Considering all together, the production of one ton of OPC clinker releases a maximum of 0.98 tons of CO_2, however the production of one ton of CSA clinker leads to a reduction, which will depend on the composition, but it can range between 0.25 to 0.40 tons of CO_2.

These CSA cements may have quite variable compositions, but all of them contain high amounts of calcium sulphoaluminate, also called Klein’s salt, ye'elimite or tetracalcium trialuminate sulphate ($C_4A_3\underline{S}$). In addition of $C_4A_3\underline{S}$ and C_2S, they may also have minor amount of phases such as CA, C_4AF, CS, $C\underline{S}H_2$ and so on and they are used due to their special applications. The properties and applications of this type of binder are strongly influenced by many factors: i) chemical and mineralogical composition of the clinker, ii) sulphate source (amount and type), iii) water to cement ratio (w/c); or iv) blending with other binders, for instance, supplementary cementitious materials (SCMs) or even OPC.

Although ye'elimite-containing cements are very promising, their use is strongly limited in Europe by the few standards concerning special cements derived from non-Portland clinkers. At the present state of European standard regulations, binders based on CSA cements cannot be used in structural concrete according to the EN 206-1; only three formulations of CSA cements – produced by Buzzi Unicemin Trino (Italy) – obtained in June 2013 a CE mark based on a ETA (European Technical Approval) procedure, released by DIBt (Deutsches Institut für Bautechnik), also allowing the use for structural application. Hence, the general aim of this PhD Thesis is to better understand (and help in the control) the behaviour of these eco-cements pastes during their hydration. Moreover, I am a member of a working group which has a large experience in anhydrous cements and clinkers characterisation by X-Ray powder diffraction combined with Rietveld methodology, and in the processing of (ceramic) materials. So, I would like to highlight my contribution in the processing and characterisation of hydrated CSA cement pastes, including the quantification of ACn (Amorphous and Crystalline not-quantified) content, and the measurement of mechanical properties (compressive strength) of the corresponding mortars.

Moreover, another objective of this PhD Thesis was to establish a methodology to prepare, store and stop hydration of cement pastes. Firstly the processing and storage of hydrated cements were optimised. Standards were followed for the paste preparation, but the curing/storing methodology has been optimised. Although initially, methacrylate sample holders were used (at 20±1ºC and 99% relative humidity) covered with a glass casing until the measured age; now hermetically closed polytetrafluoroethylene (PTFE) cylinder shape moulds are used and rotated at 15 rpm during the first 24 hours at 20±1ºC; these samples are demoulded after

24 h and stored within deionised water at 20±1ºC until the age of study. Hence, we have achieved homogenous cement pastes avoiding the undesired drying effect during hydration, or carbonation. Additionally, a methodology to stop hydration was established to further characterize the CSA cement pastes, consisted on filtration the sample with acetone twice and finally with diethyl ether.

In order to use the minimum amount of sample (laboratory studies) in mortars compressive strength measurements, moulds with dimensions of 30x30x30 mm^3 were used. Firstly these moulds were made of silicone, but those ones made of steel yielded to much more reproducible results. To compare these data with those obtained using the moulds with dimensions that fulfil the normative, the appropriate conversion factor is used.

The quantitative phase analysis of cements, and also of their hydration products, is an essential part of the research process needed to better understand their hydration behaviour and thus how their performances can be modified for any given application. In fact, this is another objective of this thesis: the correlation between the phase assemblage during hydration and their final performance. X-ray diffraction coupled with Rietveld analysis is a suitable method to obtain quantitative phase analysis of these materials in the laboratory. This methodology allows direct quantification of crystalline material. However, to quantify the amorphous or disordered materials, indirect methods are required.

Anhydrous cement samples are mainly crystalline materials although they may contain non-negligible amounts of amorphous/subcooled phases. However, hydration products can be amorphous or crystallochemically disordered. This is the reason why the quantification of the amorphous/sub-cooled phases is an important issue to understand hydration mechanisms. Amorphous content includes all amorphous phases without long range periodic order but also misfitting problems of the analyzed crystalline phases (disordered) and any crystalline phase non-included in the Rietveld control file, and it will be named hereafter Amorphous and Crystalline not-quantified (ACn). In previous studies, we used internal standard method in reflection geometry to calculate the ACn content with good results. However, the addition of an internal standard may alter the cement hydration reactions, dilute the phases in the pastes, and produce microabsorption problems and so on. Hence, have analyzed and compared studies with external standard in reflection geometry and with internal standard in transmission geometry. We can conclude that the increase of the ACn content in a mixed powder can be followed using both, internal and external standard, where the latter is of even greater utility in the study of hydration of cement pastes. This method has the inherent benefit of using common experimental requirements of LXRPD (knowing the diffractometer constant) and moreover, the sample is not altered/diluted by introducing any internal standard. On the other hand, the internal standard methodology in transmission geometry is useful to corroborate and scale the values obtained by the external standard methodology (reflection geometry). Internal standard analysis in transmission allowed us to derive ACn contents that were less biased because the particle averaging statistics were enhanced. However, this approach is not very suitable for following ACn evolution in a process because it is experimentally tedious due to the addition of the internal standard and the sample loading in the LXRPD sample holders.

Then, raw materials used in this Thesis are listed: a commercial Calcium sulphoaluminate clinker (CSA), industrially produced in China and marketed in Europe by BELITH S.P.R.L. (Belgium). Calcium sulfoaluminate cements were prepared by mixing the CSA clinker with commercial micronized natural gypsum also marketed by BELITH S.P.R.L. In some case, anhydrite and bassanite were used in cement preparation, which were prepared by heating the as received gypsum at 90ºC for 48 h and at 700ºC for 1 h, respectively. As a supplementary cementitious material (SCM) class F fly ash (FA), ASTM C618, from the power station of Lada (Spain) was used. In addition, three additives were used: i) policarboxilate; ii) tartaric acid and iii) nitrilotris(methylene)phosphonic acid. The first one was also used as superplasticizer.

The first step was to study the effect of different parameters on the hydration of cement pastes and mortars: the amount of gypsum, the water/cement (w/c) ratio, the optimum content of superplasticizer and the possible addition of fly ash. The study was undertaken by the study of the rheological behavior, the hydration process (including the evolution of the conductivity and temperature) and porosity of cement pastes and mechanical properties of corresponding mortars.

Optimum w/c ratio must be high enough to have a high degree hydration of cement phases, and to provide workability (low viscosity values), but in turn, it should be low enough to yield good mechanical strengths. The use of the optimum type and amount of additives improves the workability of cement pastes, allowing the use of lower w/c ratios and, consequently, higher compressive strength values can be obtained.

The optimised amount of gypsum to prepare CSA cements has been determined to be close to 25 wt%. Cements/mortars with higher quantities of AFt (ettringite) develop higher mechanical strengths; the stoichiometric amount of gypsum required to react with ye'elimite to form AFt in this CSA clinker is close to 30 wt%; lower amounts of gypsum (20 wt%) reacts completely and the remaining $C_4A_3\underline{S}$ is dissolved in water with the precipitation of calcium monosulphoaluminate hydrate (AFm). Conversely, greater amounts of gypsum (>30 wt%), leave unreacted gypsum without providing mechanical strength. Therefore, we were able to correlate the phase assemblage of CSA cement pastes with compressive strength values of corresponding mortars.

Another aim of the Thesis has been the cost reduction of CSA cement and the study of the possible pozzolanic effect when the cement is partially replaced by fly ash. Although the hydration of the corresponding cement pastes and the mechanical strength of mortars did not show enough evidences of pozzolanic effect (reaction between fly ash and gibbsite) even after 6 months of study, we found that the partial substitution has two main effects on the mechanical properties of mortars: i) filling effect and ii) diluting effect. The first increases slightly the compression strengths of the corresponding mortars, when 15 wt% cement is replaced by FA; independently on the water/cement (w/c=0.50 or 0.65) ratio used. However, the dilution effect predominates when substituted 30 wt% of cement, which has a negative effect on the mechanical strengths. For a fixed water/binder ratio, the compressive strengths of mortars decrease by increasing the amount of FA, mainly due to the higher water/CSA ratio, which causes higher porosity. The partial substitution of cement by 15 wt% of FA involves economic and environmental benefits. Moreover, the phase assemblage evolution during hydration is the same in the presence or in the absence of FA, suggesting that durability is not compromised.

The construction industry often requires cements, including eco-cements, with tailored properties. The knowledge and control of CSA cement hydration and properties of their respective mortars make possible the production of tailored cements and in the future, to comply all European standards for structural large-scale application.

Through the use of different kinds of sulphate sources, w/c ratios and additives additions, the rheological behaviour and setting times of cement pastes have been controlled and modified while high compressive strength values were maintained/improved.

Moreover, the effects of different additives (retarders) in bassanite pastes and mortars were studied. This was carried out by studying the rheological behaviour and hydration process (phase assemblages, heat evolution and conductivity) of the cement paste and by compression strength and expansion/retraction of the corresponding mortars.

Each sulphate source (gypsum, bassanite or anhydrite) provides mortars with different setting times, as a consequence of their different rate of solubility (0.88, 0.24 and 0.21 g/100 mL for bassanite, gypsum and anhydrite at 20 ºC, respectively). Hence, the use of different sulphate sources is a key point to control the rate of cement hydration.

On the one hand, bassanite solubility in water is very high thus, when added to cements/mortars it yields to short setting times (~20 min) that produces heterogeneous mortars with low mechanical strengths. However, the use of the optimum amount and type of additive, such as retarders or superplasticizers, setting time delays and allows the preparation of mortars with values of compressive strength up to 80 MPa at 7 days of hydration.

On the other hand, anhydrite dissolves slowly so, at 1 hydration-day, the amount of ettringite formed (~20 wt%) is lower than that in gypsum pastes (~26 wt%), producing mortars with lower compressive strengths (40.7 and 21.2 MPa, respectively with w/c=0.50). However, after 3 hydration-days, similar ettringite contents are produced but mechanical strengths of anhydrite-pastes are slightly higher than those of gypsum-pastes. This behaviour is mainly due to a higher plasticity of anhydrite-paste to better accommodate the precipitation of ettringite. This higher plasticity is due to the slower rate of dissolution of anhydrite yielding longer setting times. In addition, it must be noted that Gypsum-w/c0.50 and

Anhydrite-w/c0.50 mortars gave compressive strength values higher than those of OPC mortars at very early ages, i.e. 3 days.

At this point, we are able to obtain tailored CSA eco-cements and mortars for different applications through the control of the hydration of these cements prepared by adjusting different parameters such as w/c ratio, type and amount of additives (superplasticizers or retarders), different sulphate sources and partial substitution of CSA by FA, with the consequent economic and environmental benefits.

Abstract (Spanish version)

Resumen

La mitigación del cambio climático implica la reducción de las emisiones de gases de efecto invernadero, en general, y del dióxido de carbono (CO_2) en particular. Cada tonelada de cemento Portland (OPC, *del inglés Ordinary Portland Cement*) produce alrededor de una tonelada de dióxido de carbono. En consecuencia, la producción de OPC supone entre el 5 y el 6% de las emisiones antropogénicas de dióxido de carbono y el 4% del calentamiento global.

Debido al impacto medioambiental de la industria de los materiales de construcción, ésta se encuentra bajo una creciente presión para reducir la energía utilizada en la producción de clínker de cemento Portland y las emisiones de gases de efecto invernadero. Además, el cemento Portland no es el aglutinante ideal para todas las aplicaciones en la construcción, ya que sufre problemas de durabilidad en ambientes particularmente agresivos. Por lo tanto, existe un interés creciente en el desarrollo, caracterización y aplicación de alternativas al cemento Portland. Una de las alternativas de más interés son los cementos basados en sulfoaluminato de calcio (CSA, *del inglés Calcium SulphoAluminate*).

Los cementos CSA se consideran materiales respetuosos con el medio ambiente, ya que en su proceso de fabricación emiten menos CO_2 a la atmósfera que el Cemento Portland Ordinario, por lo que se les asigna la etiqueta "eco-cementos”. Las emisiones de dióxido de carbono de la industria de fabricación de cemento se pueden clasificar en dos grandes grupos: las que proceden de las reacciones de las materias primas y las derivadas de los procesos de operación (moliendas, funcionamiento del horno, etc.). Las materias primas y los productos obtenidos durante el proceso de clinkerización son bien conocidos. Por ejemplo, la producción de una tonelada de clínker OPC compuesto por 65% en peso de C_3S, 15% en peso de C_2S, 10% en peso de C_3A y 10% en peso de C_4AF libera 0,54 t de

dióxido de carbono. Sin embargo una tonelada de clínker CSA compuesto por 65% en peso de $C_4A_3\underline{S}$, 20 % en peso de C_2S, 9% en peso de $C\underline{S}$ y 6% en peso de C_4AF libera 0,27 t de CO_2. En consecuencia, se calcula una reducción de las emisiones de dióxido de carbono en un 49% debido a la descomposición de materia prima.

Además, la producción de cemento es un proceso de alta demanda energética, por lo que es importante tener en cuenta las emisiones procedentes del consumo de combustible para alcanzar las temperaturas de clinkerización en los hornos y así cuantificar las emisiones de CO_2. Sin embargo, esto no es una tarea fácil ya que está directamente relacionada con el equipo y el combustible empleado. Varios estudios estiman una liberación de ~0,28-0,34 toneladas de CO_2 por tonelada de clínker OPC producido cuando se emplea carbón como combustible del horno. La reducción de las emisiones de CO_2 procedentes del proceso de clinkerización se puede alcanzar mediante el uso de diferentes estrategias, como la reducción de la temperatura de clinkerización. Este es el caso de los clínkeres CSA, ya que su clinkerización se produce a ~1250ºC, lo que supone unos ~200ºC menos que la de la producción de OPC, con la consecuente reducción de hasta 0,04 toneladas de CO_2 por tonelada de clínker de CSA producido.

Las emisiones de CO_2 derivadas del consumo de energía eléctrica para la molienda en la producción de clínker de OPC no son despreciables. De hecho, se liberan 0,09 toneladas de CO_2 por tonelada de clínker producido, suponiendo que la electricidad se produce por la quema de combustibles fósiles. El hecho de producirse el CSA a temperaturas de clinkerización inferiores conduce a un clínker que es generalmente más fácil de moler, por lo que eso también supone un ahorro energético. Por ello, se estima una reducción en el consumo de electricidad que supone 0,02 toneladas menos de CO_2 emitido a la atmósfera.

Teniendo en cuenta todos estos aspectos, la producción de una tonelada de clínker OPC libera un máximo de 0,98 toneladas de CO_2. Sin embargo, la producción de una tonelada de clínker CSA conduce a una reducción, que dependerá de la composición, y que puede variar entre 0,25 a 0,40 toneladas de CO_2.

Aunque estos cementos CSA pueden presentar una composición muy variable, todos ellos contienen una elevada cantidad de sulfoaluminato de calcio, también llamado yeelimita o sal de Klein, cuya fórmula, expresada en la nomenclatura del cemento, es $C_4A_3\underline{S}$. Principalmente contienen $C_4A_3\underline{S}$ y C_2S, aunque también pueden presentar componentes minoritarios tales como CA, C_4AF, $C\underline{S}$, $C\underline{S}H_2$. Estos cementos se utilizan para aplicaciones especiales, y sus propiedades y por lo tanto aplicaciones están fuertemente influenciadas por los siguientes factores: i) composición química y mineralógica del clínker, ii) fuente de sulfato (cantidad y tipo), iii) relación agua a cemento (a/c); iv) mezcla con otros componentes, por ejemplo, materiales suplementarios de cemento (SCMs, *del inglés Supplementary Cementitious Materials*) o incluso OPC.

Aunque los cementos que contienen yeelimita son muy prometedores, su uso está muy limitado en Europa por la escasez de normas relativas a los cementos especiales derivadas de clínker distinto del Portland. Actualmente, no se pueden utilizar en el hormigón estructural cementos basados en CSA de acuerdo con la normativa EN 206-1; tan sólo tres formulaciones producidas por Buzzi Unicemin Trino (Italia) de cementos CSA han recibido recientemente la calificación adecuada para aplicaciones estructurales, concretamente en junio de 2013 han obtenido la calificación CE, en base a un procedimiento ETA (*del inglés European Technical Approval*), publicado por DIBt (Deutsches Institut für Bautechnik). Por lo tanto, el objetivo principal de esta tesis ha sido optimizar y comprender el comportamiento de estos eco-cementos ricos en ye'elimita. Además, pertenezco a un grupo de trabajo que tiene una gran experiencia en la caracterización de clínker y cementos anhidros por difracción de polvo de rayos X combinada con la metodología Rietveld, y en el procesado de materiales (cerámicos). Por ello, me gustaría destacar a su vez mi contribución en el procesado y caracterización de pastas de cemento CSA hidratadas, incluyendo la cuantificación del material amorfo y cristalino no cuantificado (ACn, *del inglés Amorphous and Crystalline non-quantified*), y la caracterización de las propiedades mecánicas (resistencia a la compresión, etc.) de los correspondientes morteros.

Además, otro de los objetivos de esta tesis doctoral ha sido establecer una metodología para la preparación, almacenamiento y tratamiento de detención de la hidratación en pastas de cemento, de forma que se obtengan resultados reproducibles. En primer lugar se optimizaron las metodologías de procesado y almacenamiento de las pastas de cemento. Se siguieron procedimientos de la normativa para la preparación de las pastas, pero la metodología de almacenamiento fue evolucionando/mejorando con el tiempo. Aunque inicialmente se utilizaron porta-muestras de metacrilato tapados con una cubierta de vidrio a 20±1°C y humedad relativa del 99% hasta el momento de su medida, en la actualidad se emplean moldes de politetrafluoroetileno (PTFE) con forma cilíndrica herméticamente cerrados. Éstos se hacen girar a 15 rpm durante las primeras 24 horas a 20±1°C; posteriormente, las muestras se desmoldan y se almacenan bajo agua desionizada a 20±1°C hasta la edad de estudio. Con este procedimiento, hemos logrado pastas de cemento homogéneas, evitando el efecto no deseado de secado durante la hidratación o la carbonatación. También, se ha establecido una metodología para detener la hidratación para la posterior caracterización de las pastas de cemento CSA, que consiste en el lavado de la muestra dos veces con acetona y un final lavado con éter dietílico.

Por otro lado, para utilizar una cantidad mínima de muestra (estudios de laboratorio) en la preparación de morteros en las medidas de resistencia a compresión, se utilizaron moldes con dimensiones de 30x30x30 mm^3. En una primera etapa estos moldes se hicieron de silicona, pero posteriormente se diseñaron de acero dando resultados mucho más reproducibles. Para comparar estos resultados con los moldes que cumplen la normativa, se emplea el factor de conversión correspondiente.

El análisis cuantitativo de fases de cementos, así como de sus productos de hidratación, es una parte esencial del proceso de investigación necesaria para entender mejor cómo se hidratan los cementos y por lo tanto, cómo se puede modificar su rendimiento para cualquier aplicación dada. De hecho éste es otro de los objetivos de esta tesis doctoral: la correlación entre el ensamblaje de fases durante la hidratación y las prestaciones finales de los cementos. La difracción de rayos X junto con el método de Rietveld son herramientas adecuadas para obtener el análisis cuantitativo de fases de estos materiales en el laboratorio. Esta metodología permite la cuantificación directa de material cristalino. Sin embargo, para la cuantificación del material amorfo o desordenado cristaloquímicamente, se requieren metodologías indirectas. Las muestras de cemento anhidro son principalmente materiales cristalinos, aunque pueden contener cantidades no despreciables de material amorfo o líquido subenfriado. Sin embargo, algunos de los productos de hidratación son amorfos o muy desordenados desde el punto de vista cristaloquímico. Por eso, es necesario cuantificar ese material amorfo para comprender los procesos de hidratación. El material amorfo incluye las fases amorfas/sub-enfriadas, sin orden a largo alcance, los problemas en el ajuste debido al desorden de algunas de las fases presentes e incluso aquellas fases cristalinas cuya descripción cristalográfica no haya sido incluida en el fichero de control en la metodología de Rietveld, por ello se denominará material amorfo y cristalino no cuantificado (ACn). En estudios previos, se obtuvieron resultados aceptables en la cuantificación de ACn utilizando la metodología de estándar interno, con difracción de rayos-X en geometría de reflexión. Sin embargo, la adición de un patrón interno puede alterar las reacciones de hidratación del cemento, diluir las fases presentes en las pastas, y producir problemas de microabsorption, etc. Por lo tanto, en esta tesis doctoral se han comparado el uso de estándar externo en la geometría reflexión y con patrón interno en geometría de transmisión. Del estudio, se puede concluir, por un lado, que el seguimiento del aumento del contenido en amorfo y materia cristalina no cuantificada sólida (ACn) en una mezcla de polvo se puede realizar mediante ambos métodos, patrón interno y externo, siendo este último el de mayor utilidad en el estudio de hidratación de pastas de cemento. Este método tiene la ventaja inherente de utilizar dispositivos experimentales comunes de difracción de rayos-X de polvo de laboratorio (LXRPD), aunque es necesario saber la constante del difractómetro, y por otra parte, la muestra no se altera/diluye mediante la introducción del estándar interno. Por otra parte, la metodología de estándar interno en geometría de transmisión es útil para corroborar los valores obtenidos por la metodología estándar externo. La geometría en transmisión mejora la distribución estadística de partículas, lo que permite obtener contenidos de ACn más exactos con el método del estándar interno. Sin embargo, esta metodología de estándar interno no es muy recomendable para seguir la evolución de ACn en muestras hidratadas, ya que requiere mezclar la muestra con el estándar interno de forma homogénea y además, la preparación de la muestra para la geometría en transmisión es, experimentalmente, muy tediosa.

A continuación se presentan las materias primas utilizadas en esta tesis doctoral: un clínker comercial de sulfoaluminato de calcio. Este clínker se produce en China y es comercializado en Europa por BELITH S.P.R.L. (Bélgica). El correspondiente cemento fue preparado en el laboratorio mezclando el clínker con yeso natural comercializado también por BELITH S.P.R.L. En algunos casos, se ha utilizado anhidrita o basanita para la preparación del cemento, las cuales se han preparado calentando el yeso comercial a 700ºC durante 1 hora y a 90ºC durante 48 h, respectivamente. Como material suplementario de cemento se ha empleado ceniza volante de clase F, según norma ASTM C618, procedente de la central eléctrica de Lada (España). Finalmente se usaron 3 aditivos retardantes basados en: i) policarboxilato; ii) ácido tartárico; e iii) ácido nitrilotris(metilen)fosfónico. El primero también fue utilizado como superplastificante.

El primer paso fue estudiar el efecto de los siguientes parámetros sobre la hidratación de las pastas de cemento y los correspondientes morteros: la cantidad de yeso, la relación agua/cemento (a/c), el contenido óptimo de superplastificante y la posible adición de cenizas volantes. El trabajo se abordó mediante el estudio del comportamiento reológico, el proceso de hidratación (incluida la evolución de la conductividad y de la temperatura) y porosidad de las pastas de cemento y finalmente se midieron las resistencias a la compresión de los morteros correspondientes.

La relación agua/cemento óptima debe ser lo suficientemente alta para que se produzca la hidratación de las fases del cemento, y proporcione suficiente trabajabilidad (bajos valores de viscosidad), pero a su vez, debe ser lo suficientemente baja para que presente resistencias mecánicas altas. El uso del tipo y cantidad óptimos de aditivos mejora la trabajabilidad de las pastas de cemento, lo que permite el uso de una menor relación a/c y, en consecuencia, los valores de resistencia a la compresión puedan ser superiores.

Por otra parte, se determinóla cantidad óptima de yeso para preparar cementos CSA, encontrándose próxima a 25% en peso. Los cementos/morteros con mayores cantidades de AFt (etringita), procedente de la reacción entre yeelimita y fuente de sulfato, desarrollaron valores de resistencia a compresión superiores; en el clínker CSA utilizado, la cantidad estequiométrica de yeso requerida para reaccionar con la yeelimita presente en el clínker es próxima a 30% en peso; cuando se adicionan menores cantidades de yeso (20% en peso), éste reacciona completamente, con lo que la yeelimita sobrante se disuelve en agua produciendo la precipitación de monosulfoaluminato de calcio hidratado (AFm), en lugar de AFt. Por el contrario, mayores cantidades de yeso (>30% en peso), nos dejaría yeso sin reaccionar sin aportar resistencias mecánicas. Por lo tanto, hemos sido capaces de correlacionar el ensamblaje de fases de las pastas de cemento CSA con los valores de resistencia a la compresión de los correspondientes morteros.

Otro objetivo de la tesis ha sido la reducción del coste del cemento CSA y el estudio del posible efecto puzolánico cuando dicho cemento es parcialmente sustituido por ceniza volante. Aunque la hidratación de las correspondientes pastas de cemento y las resistencias mecánicas de los morteros no mostraban indicios suficientes del efecto puzolánico (reacción entre cenizas volantes y gibbsita), incluso tras 6 meses de estudio, podemos afirmar que dicha sustitución parcial tiene dos efectos principales sobre las propiedades mecánicas de los morteros: i) efecto de relleno y ii) efecto de dilución. El primero aumenta ligeramente las resistencias a la compresión de los correspondientes morteros, cuando 15% en peso del cemento es sustituido por cenizas volantes; esto sucede independientemente de la relación agua/cemento (a/c=0,50 o 0,65). Por el contrario, el efecto dilución predomina cuando se sustituye un 30% en peso del cemento, con el consiguiente efecto negativo en las resistencias mecánicas. Para una relación agua/sólido fija, las resistencias a la compresión de los morteros disminuyen al aumentar la cantidad de cenizas volantes, debido principalmente a la relación a/c más alta, lo que provoca mayor porosidad. La sustitución parcial del cemento en un 15% en peso de cenizas volantes implica beneficios económicos y ambientales. Por otra parte, la evolución del ensamblaje de fases durante la hidratación es el mismo en presencia o en ausencia de cenizas volantes, lo que sugiere que la durabilidad no se verá comprometida.

Resumen

Con frecuencia, la industria de la construcción requiere cementos, o eco-cementos, con propiedades pre-establecidas. El conocimiento y control de la hidratación de cementos CSA y de las propiedades de sus correspondientes morteros a medio/largo plazo permiten el diseño de “cementos a la carta”; esto hace posible que, en un futuro, puedan cumplir todas las normativas europeas para su aplicación estructural a gran escala.

A través del uso de diferentes tipos de fuentes de sulfato, la relación agua/cemento y la adición de diferentes aditivos, se ha controlado y modificado el comportamiento reológico de las pastas y su tiempo de fraguado a la vez que se ha controlado el ensamblaje de fases y mantenido/mejorado los altos valores de resistencia a la compresión.

El estudio del efecto de diferentes aditivos (retardantes) en pastas y morteros con basanita se abordó mediante el control del comportamiento reológico y del proceso de hidratación (ensamblaje de fases, calor desprendido y conductividad) de las pastas de cemento y a través de las resistencias a la compresión y expansión / retracción de los correspondientes morteros.

En el caso del estudio de las diferentes fuentes de sulfato, cabe destacar que, como consecuencia de la diferente solubilidad de las diferentes fuentes de sulfato (0,88, 0,24 y 0,21 g/100ml para basanita, yeso y anhidrita a 20°C, respectivamente), se obtuvieron morteros con diferentes tiempos de fraguado. Por lo tanto, el uso de diferentes fuentes de sulfato es un punto clave para controlar la velocidad de hidratación del cemento y las prestaciones a edades tempranas. Por un lado, la solubilidad de la basanita en el agua es la más alta, por lo que cuando se añade a los cementos / morteros obtenemos tiempos de fraguado muy cortos (~20 min), produciéndose morteros heterogéneos con resistencias mecánicas bajas. Sin embargo, el uso de la cantidad y tipo de aditivo óptima, como retardantes o

superplastificantes, retrasan el tiempo de fraguado y permite la preparación de morteros con valores de resistencia a la compresión de hasta 80 MPa a los 7 días de hidratación. Por otro lado, la anhidrita es la que se disuelve más lentamente, formándose después de 1 día de hidratación menor contenido de AFt que en el caso de las pastas de yeso (~20% en peso y ~26% en peso, respectivamente), afectando a los valores de resistencia a la compresión de los correspondientes morteros (40.7 y 21.2, respectivamente, cuando a/c=0,50). Sin embargo, después de 3 días de hidratación, aunque el contenido de ettringita en ambas pastas es similar, las resistencias mecánicas de los morteros con anhidrita son ligeramente superiores a las de los morteros con yeso. Este comportamiento se debe principalmente a la mayor plasticidad de las pastas con anhidrita debida a su menor velocidad de disolución y mayor tiempo de fraguado, lo que permite que la ettringita precipitada se acomode mejor. Además, hay que señalar que los morteros de yeso-a/c=0.50 y de la anhidrita-a/c=0.50 dieron valores de resistencia a la compresión superiores a los de los morteros de OPC a edades muy tempranas (3 días).

En este punto, estamos en condiciones de obtener eco-cementos CSA y sus correspondientes morteros “a la carta” para diferentes aplicaciones a través del control de la hidratación de estos cementos preparados mediante el ajuste de diferentes parámetros: relación agua/cemento, tipo y cantidad de aditivos (superplastificantes o retardantes), diferentes fuentes de sulfato y la sustitución parcial de cemento por cenizas volantes, con los consecuentes beneficios económicos y ambientales.

1. Introduction

1. Introduction to cements

Blezard (2004) describes cements as adhesive substances capable of uniting fragments or masses of solid matter to a compact whole. This term can be used for almost any type of binder with chemistry ranging from fully organic to totally inorganic compounds. We are interested in inorganic cements, those based in inorganic compounds and the basic ingredient of concretes and mortars for construction applications, which work as a kind of glue to stick sand and gravel together; this cement is used as poorly-soluble but highly-reactive powders in water.

In addition, cement is defined (standard UNE-EN 197-1=2011) as a hydraulic binder, i.e. a finely divided inorganic material that when is mixed with water, forms a paste that sets and hardens by means of reactions and processes of hydration and after hardening, retains its strength and stability even under water. Moreover, mortars can be described as materials made by mixing cement, fine aggregate and water; and concretes are materials prepared by mixing cement, coarse aggregates, fine aggregate and water, either with or without the addition of additives and additions.

Throughout history, cementing construction materials have played a vital role (www.oficemen.com). They were used widely in the ancient world. The first use of cement-related materials can be placed in the Egyptian civilization. They used lime, obtained by heating gypsum ($CaSO_4 \cdot 2H_2O$; $C\underline{S}H_2$), limestone (LS; $CaCO_3$; $C\underline{C}$) or chalk, as a bonding agent in their constructions, for example, in the Cheops pyramids (approx. 2589-2566 B.C.). In addition, Greek (800 B.C.) and Roman (100 B.C.) civilizations developed the use of aluminosilicates mixed with volcanic origin limes obtaining mortars with better final performances than those used by Egyptians. This type of mortar was used to construct some of the architecture wonders of ancient Rome, including the Coliseum. Nowadays these Roman cements are still used and called pozzolanic cements. Until the seventeenth century (A.D.) a significant technological progress was not observed. But the beginning of the cement development happened in 1824 when Joseph Aspdin created and patented Ordinary Portland cement (OPC), which name comes from the similarity between this material and the limestone of Portland (County of Dorset, UK). This cement was only hydraulic lime, but this patent opened the way to the development of calcium silicate cements that we know today.

Nowadays, Ordinary Portland Cement is the most used building material, which has become the dominant binder used in the preparation of concrete for construction applications. Portland cement is now prepared by heating a mixture of limestone and clay, or other materials of similar composition and sufficient reactivity, at a temperature of ~1450ºC (Taylor 1997). Partial fusion occurs, and nodules of clinker are produced. The cement is finally prepared by grinding the clinker and mixing it with finely ground calcium sulphate, which will control the setting time. It is commonly described as gypsum, but this may be partly or wholly replaced by other forms of calcium sulphate. Some specifications allow the addition of other materials at the grinding stage.

1.1. Cement manufacture

1.1.1. Cement manufacturing process

Cement manufacturing process can be gathered into four steps: i) selection of raw materials; ii) grinding, homogenization and preparation of raw materials; iii) clinkering and iv) grinding clinker with other components. All these steps are described below.

i) Selection of raw materials

In general, any mineral or industrial by-product containing lime, silica, alumina and iron oxide can be used as raw material (Vazquez and Gutierrez-Jimenez 2001). Limestone materials are widely used as sources of lime in the clinker manufacturing due to its high content in calcium carbonate. Chalk is a geologically sedimentary rock, younger than limestone, which is a cheaper exploitation due to its high porosity. Clays and shale are products of alkaline and alkaline earth silicates weathering; they present the follow approximated chemical composition: SiO_2 (55-60 wt%), Al_2O_3 (15-25 wt%), Fe_2O_3 (5-10 wt%) and they may also have small amounts of MgO, alkaline oxides, water and other components. Clays combine one or more clay minerals traces of metal oxides with iron and other impurities and also organic matter, which provides with a yellow red coloration. In the OPC production, iron rich clays are needed, which also will provide with the required amount of Al_2O_3 and Fe_2O_3.

Other materials are usually added in small proportions to the clay and limestone mixtures in order to obtain the final desired composition (Gomá 1979). In this way, bauxites that can contain up to 60 wt% of Al_2O_3 are used to increase the amount of Al_2O_3; sands provide with silicon (in quartz form) with low reactivity which difficult the raw material clinkering (described below). Diatomites are sedimentary rocks which have high SiO_2 and low iron contents, and are more reactive than sands; hence it is also widely used. Furthermore, kaolin sands can also contain ~7-12 wt% of Al_2O_3 in their composition. The additional required iron, iron ore, roasted pyrites ash, and so on, are commonly used.

A typical raw material for a common Portland clinker can be prepared with 80 wt% limestone, 19 wt% clay, and other materials (1 wt%), such as Fe_2O_3.

In addition, the feedstock material can be in dry, semi-dry (15-20 wt% of water) or damp (30-40 wt% of water) state. For the latter, the material is prepared by wet milling (wet process). The most favourable thermal balance happens for the dry process, although the power required is higher due to the milling.

ii) Grinding, homogenization and preparation of the raw materials

Raw materials are ground up to show the desired particle size distribution and homogenization.

Before being introduced into the kiln, the raw meal is heated in counter flow heat exchanger with gases from the kiln where the raw materials can suffer a partial reaction (e. g. decarbonation). Thus, preheated raw meal is introduced in the kiln by one of the ends and progresses slowly toward the opposite end owing to the continue rotation movement (1-4 rpm) and to the slight tilt (3-4%) from the horizontal, in the dry process.

iii) Clinkering

This is the process where the ground and homogenized raw materials are heated at a temperature about ~1450°C (it depends on the composition) during 10-15 minutes to form clinker. Several chemical reactions, mainly in the solid-liquid interface take place in this process. Figure 1.1. shows a schematic diagram of a rotatory kiln, including the main stages occuring inside in OPC manufacture.

Clinker is obtained in modules (3-20 mm diameter) in a semi-solid state (in the clinkerization area) and solidifies completely in the cooling zone. This process has a great influence on the microstructure of material, mineralogy, grindability, etc.

As an example, an OPC clinker presents a typical chemical composition of 67 wt% of CaO, 22 wt% of SiO_2, 5 wt% of Al_2O_3, 3 wt% of Fe_2O_3, and 3 wt% of other minor oxide components. It usually contains four major phases: 50-70 of wt% alite (C_3S), 15-30 wt% of belite (C_2S), 5-10 wt% of tricalcium aluminate (C_3A) and 5-15 wt% of tetracalcium aluminoferrite (C_4AF). Several other minor phases, such as alkaline sulphates and/or calcium oxide, are normally found as minority phases (Gielen and Tanaka 2006; Alaoui et al. 2007).

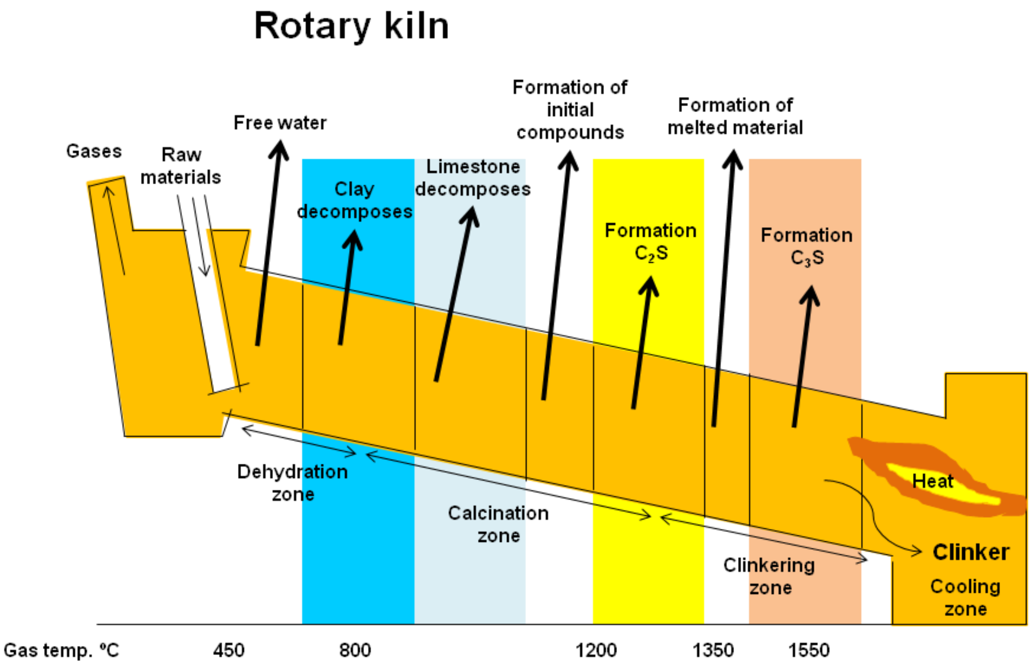

Figure 1.1. Schematic diagram of rotary kiln, including the main stages occuring inside in OPC manufacture.

iv) Grinding clinker with other components

The clinker is mixed with a sulphate source, which acts as set regulator, to form cement.

The set regulator serves to retard the induction hydration period, and it depends on the type and amount (described below) of the sulphate source (Pelletier-Chaignat et al. 2012; Glasser and Zhang 2001; Pera and Ambroise 2004). They usually form a precipitate which coats the grains of cement or even reduce the solubility of the cement hydratable components.

Gypsum is commonly used as set regulator. OPC cements usually have approx 5 wt% sulphate to avoid a reaction of aluminates with water. Commercial gypsum may also contain anhydrite ($CaSO_4$; $C\underline{S}$), quartz (SiO_2) and/or limestone in its formulation.

When gypsum or bassanite ($CaSO_4 \cdot 0.5H_2O$; $C\underline{S}H_{0.5}$) are used as set regulators, the temperature of this cement grinding step must be kept under control to prevent severe dehydration. This is carried out with a cold air circulation and/or water diffusers.

Furthermore, other materials are usually added, such as fly ash (FA), blast furnace slag (BFS), limestone, pozzolan, and so on. The mixture needs to be ground and homogenized.

During the hydration of cements (as it happens in OPC), some additions with pozzolanic properties such as fly ash and silica fume (SF) can react with the calcium hydroxide that is generated from silicates hydration to form insoluble products; others named hydraulic aids, such as blast furnace slag can react directly with water to produce cohesive reaction products (Vazquez and Gutierrez-Jimenez 2001). The addition of by-products provides with special features to cement, but moreover there are other important reasons for their use: the use of waste materials, the consumption energy reduction, the reduction of the CO_2 footprint and the cement cost manufacture reduction.

The cement is usually classified according to its composition and final properties (Standard UNE-EN 197-1=2011).

1.1.2. Energy consumption and CO_2 emissions

Annual worldwide Portland cement production is approaching 4 Gt (U.S. Geological Survey 2014). Figure 1.2. shows the OPC production in the period 2001-2012. From the year 2008, due to the crisis in the sector, a decrease occurs in the cement production in most countries; however, continents with a clear economic growth such as Asia and Africa keep increasing the cement production (www.cembureau.be).

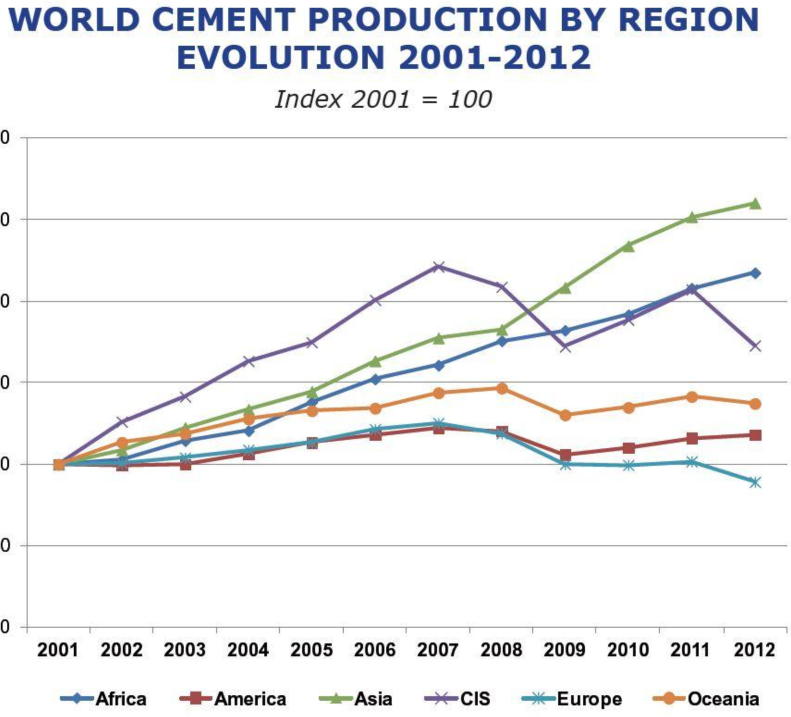

Figure 1.2. World cement production by region evolution 2001-2012.

OPC manufacturing consumes 10-11x10^{18} J of energy annually, approximately 2-3% of global primary energy use. The theoretical heat formation of 1 kg of clinker, using common raw materials, is about 1750 kJ (Taylor 1997).

Furthermore, the main disadvantage of this process is the emission of greenhouse gases. Principal gases emitted (Table 1.1.) are nitrogen from air combustion, CO_2 and water, from raw materials and combustion process, and oxygen. A small amount of solid particles, SO_2, NO_x, CO, and in less quantity, chlorides, organic compounds and heavy metals are also emitted.

Table 1.1. Main gases emitted in the clinkering kiln (Cuberos 2011).

Gases	**Emissions (vol%)**
Nitrogen (N_2)	46-66
Carbon dioxide (CO_2)	11-29
Water (H_2O)	10-39
Oxygen (O_2)	4-12
Rest	<1

All these gases are dusted in filters before being emitted into the atmosphere. Particles and sulphur oxides cement industry emissions are not significant for climate change; NO_x emissions from the cement industry are also not significant, but can be locally annoying. In contrast, CO_2 cement industry emissions are very important. Thus, most of the emissions are due to the fossil fuel and biomass burning (McCaffrey 2002). Every ton of Portland cement production results in more than 0.85 t of carbon dioxide (CO_2) (McCaffrey 2002; Damtoft et al. 2008); consequently, OPC production accounts for 5-6% of anthropogenic carbon dioxide emissions (McCaffrey 2002; Damtoft et al. 2008; Barcelo et al. 2014) and for approximately 4% of total global warming (McCaffrey 2002). Also, most of the produced cement is intended to obtain concrete and mortars, therefore we must take into account the energy consumed in the materials mixture and transport.

Thus, for each ton of concrete also are emitted 0.08 t CO_2 into atmosphere (Gartner 2004).

Due to these environmental problems the industry of building materials is under increasing pressure to reduce the energy used in production of Portland cement clinker and the associated greenhouse gas emissions. Moreover, Portland cement is not the ideal binder for all construction applications, as it suffers durability problems in particularly aggressive environments. Hence, there is a growing interest in the development, characterization, and implementation of alternatives to Portland cements as a binders in concretes. The interest in **ye'elimite-containing cements** are increasing as are **eco-friendly materials because their manufacture process releases less CO_2 into atmosphere** than ordinary Portland cement (Sharp et al. 1999; Gartner 2004; Barcelo et al. 2014). This reduction depends on the composition, but it can release up to 40% less CO_2 emissions. This is described below.

1.2. Ye'elimite-containing cements

Since 1970s commercial ye'elimite-containing cements known as Calcium sulphoaluminate (CSA) cements have been manufactured and used on a large scale in China (Zhang et al. 1999). CSA cements are/were known as “the third series cements of China” (the first series being OPC and the second series being CAC, Calcium Alumina Cements) with special applications such as high strength developments at early-ages used in precast concrete and at moderate curing temperatures (Quillin 2001; Glasser and Zhang 2001), self-stressing materials (Péra and Ambroise 2004; Georgin et al. 2008), with expansive properties for shrinkage compensating concrete (Klein 1963; Chen et al. 2012) or for radioactive element encapsulation in high-density cement pastes (Zhou et al. 2006; Cau Dit Coumes et al. 2009; Sun et al. 2011).

These binders may have quite variable compositions, but all of them contain high amounts of ye'elimite ($C_4A_3\underline{S}$), also called Klein’s salt, calcium sulphoaluminate or tetracalcium trialuminate sulphate (Odler 2000). So, the main phases are $C_4A_3\underline{S}$ and C_2S and also they have minor amount of phases such as CA, C_4AF, CS, $C\underline{S}H_2$ (Sahu and Majling 1993) and they are used due to their special applications. The properties and applications of this type of binder are strongly influenced by many factors: i) chemical and mineralogical composition of the clinker; ii) sulphate source (amount and type); iii) water to cement ratio (w/c); or iv) blending with other binders, for instance, OPC.

1.2.1. Classification

Although ye'elimite-containing cements are very promising, their use is limited in Europe by the few standards concerning special cements derived from non-Portland clinkers. At the present state of European standard regulations, binders based on CSA cements cannot be used in structural concrete according to the EN 206-1; only three formulations of CSA cements – produced by Buzzi Unicemin Trino (Italy) – obtained in June 2013 a CE mark based on a ETA (European Technical Approval) procedure, released by DIBt (Deutsches Institut für Bautechnik), also allowing the use for structural application (Paul et al. 2015). There are very wide ranges of phase assemblages in ye'elimite-containing cements (Zhang et al. 1999; Quillin 2007) and that need to be clarified. These eco-cements can be classified according to the content of their main crystalline phase. Aranda and De la Torre (2013) proposed to unify the terminology used for these cements, see Table 1.2. The most representative cements of table 1.2. are described below:

i) CSA

Calcium Sulpho-Aluminate (**CSA**) cements which refer to those with high $C_4A_3\underline{S}$ contents, are prepared from CSA clinkers containing 50-80 wt% of $C_4A_3\underline{S}$ (Zhang et al. 1999; Sahu and Majling 1993; Older 2000; Glasser and Zhang 2001). These clinkers may also have minor phases such as C_2S, CT, C_4AF, $C\underline{S}$ and others. The calcium sulphate addition is very important as it may profoundly affect the properties of the resulting binder (Winnefeld and Barlag 2010; Bergel et al. 2011a and Chen et al. 2012). The calcium sulphate source and content have to be customized for a given application. These cements can be used alone or in combination with other cements to provide an improved early resistance (they can show mechanical strengths higher than 80 MPa at 7 days), low shrinkage, high impermeability, and a strong resistance to sulphate attack. Unfortunately due to the high amount of expensive aluminum source needed in their productions, CSA clinkers cannot replace OPC in massive constructions. Al_2O_3 and SO_3 contents in CSA usually range between 30-40 and 8-14 wt%, respectively. Al_2O_3 contents will be further discussed below.

This is the a highly promising ye'elimite containing cement, since its production releases the lowest CO_2 emissions, and show the best higher mechanical strengths. This thesis is focused on this type of cement, hence it will be deeper described below.

ii) BCSA

Belite Calcium Sulpho-Aluminate (**BCSA**) term is reserved to the cements arising from clinkers containing C_2S (belite) as the main phase (40-50 wt %) and intermediate $C_4A_3\underline{S}$ contents (20-30%). Due to the high amount of C_2S, these materials showed mechanical strengths up to 50 MPa at 28 days. These cements,

Table 1.2. Ye'elimite-containing cements (Aranda and De la Torre 2013).

Acronym	Definition	Main phase	Second & other phase(s)
CSA	Calcium Sulpho Aluminate cement	$C_4A_3\underline{S}$	C_2S (C_4AF, $C\underline{S}$, CT, ...)
BCSAF	Iron-rich Belite Calcium Sulpho Aluminate cement	C_2S	$C_4A_3\underline{S}$ (C_4AF, CT, …)
BCSAA	Aluminum-rich Belite Calcium Sulpho Aluminate cement	C_2S	$C_4A_3\underline{S}$ ($C_{12}A_7$, CA, …)
ACSA	Alite Calcium Sulpho Aluminate cement	$C_4A_3\underline{S}$	C_3S (C_2S, …)
SAC	Sulpho Aluminate Cement	analogous to CSA	Zhang et al. 1999
BSA	Belite Sulpho Aluminate	analogous to CSA	Older 2000
CSAC	Calcium Sulpho Aluminate Cement	analogous to CSA	Glasser and Zhang 2001
SCC	Sulpho Aluminate Cement Clinker	analogous to CSA	Fu et al. 2003
FAC	Ferro Aluminate Cement	Iron-reach CSA	Zhang et al. 1999
SFAB	Sulpho Ferro Aluminate Belite	Iron-reach CSA	Older 2000
SAB	Sulpho Aluminate Belite	analogous to BCSAF	Janotka et al. 2007
BSAF	Belite Sulpho Aluminate Ferrite	analogous to BCSAF	Older 2000
SAC	Sulpho Aluminate Cement	analogous to CSA	Zhang et al. 1999
BSA	Belite Sulpho Aluminate	analogous to CSA	Older 2000

also known as sulphobelite and are a new emerging type of ye'elimite-containing cement due to their environmental benefits.

The most common formulation of BCSA clinkers consists on β-C_2S, $C_4A_3\underline{S}$ and C_4AF (Janotka and Krajci 1999; Janotka et al. 2007; Adolfsson et al. 2007). Also termed iron-rich BCSA (**BCSAF)**, they are produced at temperatures close to 1250 ºC and show a rapid hardening, excellent durability, self-stressing and volume stability, depending on the amount of gypsum added (Pera and Ambroise 2004). It must be highlighted that BCSAF clinkers do not belong to “the third series cement of China” (CSA), which have much higher amounts of ye'elimite, to avoid confusion. These cements are being studied with the final aim of replacing OPC as the aluminum demand is much smaller. Al_2O_3 and SO_3 contents in BCSAF usually range between 14-17 and 3.5-4.5 wt%, respectively (Aranda and De la Torre 2013).

Aluminum-rich BCSA (or **BCSAA**) clinkers with C_2S, $C_4A_3\underline{S}$, $C_{12}A_7$ and CA as main phases (Martín-Sedeño et al. 2010; and references therein) are prepared in order to further enhance mechanical strengths at very early ages, C_4AF phase may be substituted by $C_{12}A_7$. Nevertheless, the clinkering temperature should be increased (around ~100ºC) and moreover, higher amounts of expensive bauxite (or another aluminum-rich source) are needed.

Those binders with high Al_2O_3 content gained 90% of their 8 day strength after 1 day of hydration, mainly due to high contents of $C_4A_3\underline{S}$, $C_{12}A_7$ and CA. On the other hand, materials with higher amounts of SiO_2 developed greater mechanical strengths after 28 days of hydration, being C_2S the responsible for this behavior (Aranda and De la Torre 2013).

iii) ACSA

To end this point, alite calcium sulphoaluminate (**ACSA**) cements are other type which would correspond to those characterized by the simultaneous presence of C_3S and $C_4A_3\underline{S}$ phases. In this special case, ye'elimite phase content may be even higher than that of alite (Li et al. 2007a). Other phases which may appear in these clinkers are C_2S, C_4AF and C_3A (Abdul-Maula and Odler 1992; Odler and Zhang 1996; Zhang and Odler 1996). However, this type of clinker is quite difficult to prepare because the optimum temperatures for the synthesis of the two phases differ considerably. Nevertheless the addition of a small amount of CaF_2 and/or CuO, TiO_2 (Li et al. 2007b; Yanjun et al. 2007; Ma et al. 2006; Liu et al. 2009) to the raw mixes allows the coexistence of both phases at temperatures between 1230 and 1300°C.

1.2.2. CO_2 emission reduction in the manufacture of ye'elimite-containing cements

These types of cements are interesting because they release less CO_2 in their manufacture when compared to OPC production. The carbon dioxide emissions can be classified in two main categories: those coming from raw materials and those from the operation processes. Table 1.3. gives CO_2 emissions related to the production of cement components calculated according to the stoichiometric of chemical reactions, for example:

$$3C\underline{C} + S \rightarrow C_3S + 3\underline{C} \qquad [1.1]$$

Reaction [1.1] is the main one in the OPC production. Therefore, the production of one ton of OPC clinker composed of 65 wt% of C_3S, 15 wt% of C_2S, 10 wt% of C_3A and 10 wt% of C_4AF released 0.54 tons of carbon dioxide, however one ton of

CSA clinker composed by 65 wt% of $C_4A_3\underline{S}$, 20 wt% of C_2S, 9 wt% of $C\underline{S}$ and 6 wt% C_4AF releases 0.27 tons of CO_2 (Figure 1.3.). In this case the most important reaction is:

$$3C\underline{C} + 3A + C\underline{S} \rightarrow C_4A_3\underline{S} + 3\underline{C} \qquad [1.2]$$

that gives CO_2 emissions from the formation of ye'elimite phase. Consequently, a reduction in carbon dioxide emissions of 49% is calculated due to raw material decomposition.

The second CO_2 emissions category is from operation processes. However, this is not an easy task as it is directly related to the type of processing equipment and the specific chosen fuel. Gartner in 2004 published an estimation of 0.28 t of CO_2 per ton of clinker produced assuming that good quality of bituminous coal is used and taking into account energy efficiency of modern kilns. However, McCaffrey (2002) states that 0.34 t of CO_2 per ton of clinker produced is released into atmosphere due to the burning of coal in the kiln. The reduction in CO_2 emissions coming from the burning of the fuel can be achieved by different strategies (Gartner 2004; Juenger et al. 2011) including the reduction of clinkering temperature. This is the case of CSA clinker production where the operating temperature can be reduced down to ~1250ºC, ~200ºC lower than that of OPC production (Phair 2006), with a concomitant reduction of up to 0.04 t of CO_2 per ton of CSA clinker produced. Moreover, CO_2 emissions derived from electricity consumption for grinding in OPC clinker production are not negligible. In fact, 0.09 t of CO_2 per ton of clinker produced are calculated, assuming that fossil fuels are used to produce the electricity (McCaffrey 2002). Since the lower firing temperatures lead to a CSA clinker which is generally easier to be ground, hence energy savings also occur in the grinding of CSA clinker compared to OPC. Therefore, reduction on the electricity consumption yields a depletion of up to 0.02 t of CO_2 emissions.

Table 1.3. CO_2 emissions per ton of component produced, considering $CaCO_3$ as calcium source.

Component	**t CO_2/t of component**
C_3S	0.58
C_2S	0.51
C_3A	0.49
C_4AF	0.36
$C_4A_3\underline{S}$	0.22

Considering all together, the production of one ton of OPC clinker releases a maximum of 0.98 tons of CO_2, however the production of one ton of CSA clinker leads to a reduction, which will depend on the composition, but it can range between 0.25 to 0.40 tons of CO_2. With the CSA composition shown in Figure 1.3., a reduction of 0.36 tons of CO_2 per ton of clinker is obtained which means a relative reduction of 37% of the CO_2 emission footprint when compared to OPC manufacturing.

1.2.3. Laboratory-prepared ye'elimite-containing cements

Broadly ye'elimite-containing clinkers are produced by mixing limestone, clay and/or bauxite and gypsum, as sources of calcium, silicon/aluminum and sulphur, respectively. Some compositions ranging ~20 wt% of $C_4A_3\underline{S}$, 25-45 wt% of C_2S, 15-40 wt% of C_4AF and 15-20 wt% of $C\underline{S}$ were reported by Mehta (1977). For BCSAF preparations, silica-rich bauxites and iron ores are used. Singh and Pradip (2008), Pace (2011), Yang (2013) and Shen (2014) discussed about the availability of waste materials containing high-amounts of alumina (such as fly ashes and aluminum anodization muds) or sulphates (such as phosphogypsum and flue gas desulfurized gypsum), since it is a key issue for the economic production of CSA cements. Even aluminum-poor wastes, such as municipal solid waste incineration fly ash, can be used as raw materials for cement preparation (Wu et al. 2011). The addition of waste materials in the raw mixtures to produce CSA and BCSAF clinkers also has been investigated by other authors (Beretka et al. 1993; Arjunan et al. 1999; Katsioti et al. 2006; Seluck et al. 2010; Viani and Gualtieri 2013). These studies concluded that these clinkers showed similar final performances strengths to those obtained with the cements prepared using common grade raw materials, i.e. setting times, consistency, expansion and mechanical properties. Senff et al. (2011) presented the use of the design of experiments for the formulation of clinkers with mineralogical composition ranging 30-70 wt% of C_2S, 20-60 wt% $C_4A_3\underline{S}$ and 10-25 wt% C_4AF and mathematical models to predict properties. They concluded that with higher amounts of $C_4A_3\underline{S}$ mechanical strength at early ages strongly increases, as expected.

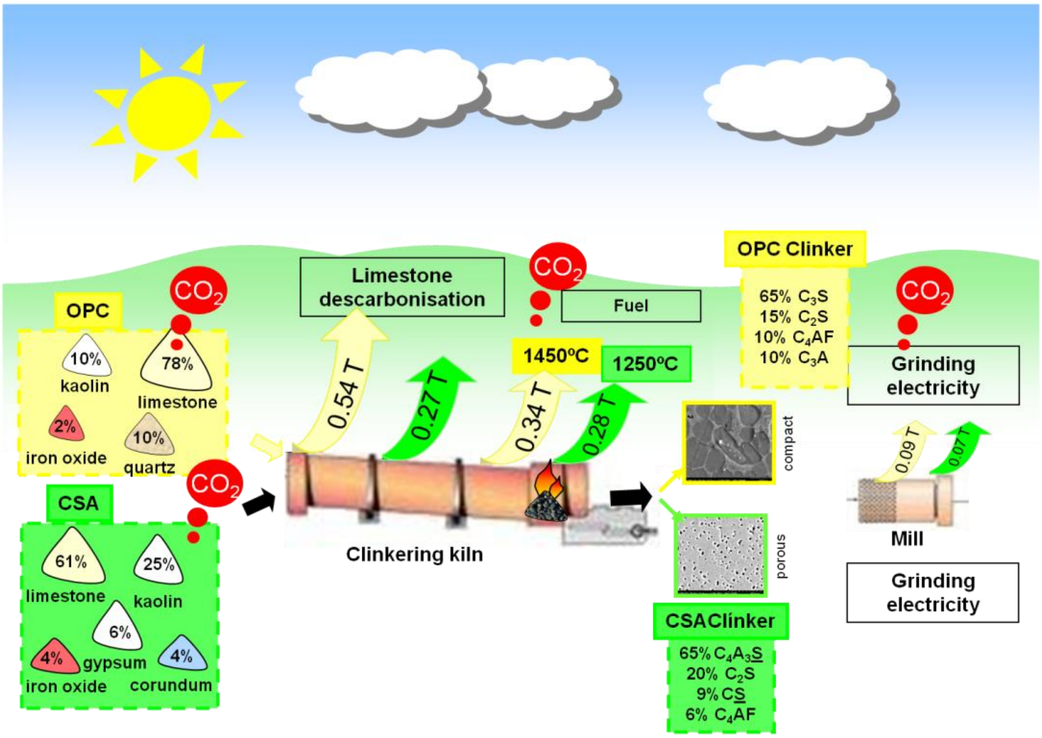

Figure 1.3. Comparison of OPC and CSA CO_2 footprint.

Ye'elimite-containing clinkers are usually prepared in rotary kilns at temperatures ranging 1250-1350ºC. Clinkering reactions slightly depends on the composition of the raw mixture. In the last decade, the research in the preparation of BCSAF clinkers has increased considerably (Sahu and Majling 1994; Arjunan et al 1999; De la Torre et al. 2011a,b; Chen et al. 2011), and concluded that, up to 900ºC, H_2O and CO_2 are released into atmosphere due to dehydration, dehydroxylation and decarbonation of the raw material. Below this temperature, phases arising from the decomposition of the raw materials, such as free lime, β-SiO_2 or anhydrite coexist with a bad-crystallized/amorphous aluminum rich phase. A High-Temperature Synchrotron X-Ray powder diffraction (HT-SXRPD) study of a BCSAF clinker activated with boron was performed to clarify the formation mechanism of these type of clinker (De la Torre et al. 2011a). Figure 1.4. shows a selected range of HT-SXRPD raw data (λ=0.3Å) at various temperatures. The diffraction peaks, arising from different phases, are labelled in order to highlight the transformations which are taking place on heating. Solid state formation of ye'elimite (open circles) has been proved to start over ~1000ºC. Recent reports (De la Torre et al. 2011a,b) have presented clinkering reactions of BCSAF clinkers with and without activators. In these studies, high resolution SXRPD was used to follow the chemical reactions with temperature during clinkering. BCSAF clinkers with 50 wt% C_2S, 30 wt% of $C_4A_3\underline{S}$ and 20 wt% of C_4AF expected mineralogical phase assemblage were prepared in-situ by mixing ~61 wt% of calcite, ~25 wt% of kaolin, ~4 wt% of alumina, ~6 wt% of gypsum and ~4 wt% iron oxide. $C_4A_3\underline{S}$ and C_4AF were formed as temperature increases, because free lime reacts with anhydrite and amorphous aluminum/iron-rich phases. Belite is also formed below 900ºC, being α'_H-C_2S, the polymorph identified at that temperature. In those experimental conditions, free lime had completely reacted at ~1100ºC, star in Figure 1.4. The system CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3 contains eighteen phases (Sahu and Majling 1993) related to BCSAF cements. However, Li et al. (2001) published that is possible to control final phase assemblage and to avoid the formation of some non-hydraulic phases such as C_2AS or $C_5S_2\underline{S}$. Belite is also formed by the decomposition of C_2AS phase at high temperature, i.e. over 1100ºC. However C_2AS may still be present in the clinker if the amount of CaO is not enough to react with SiO_2.

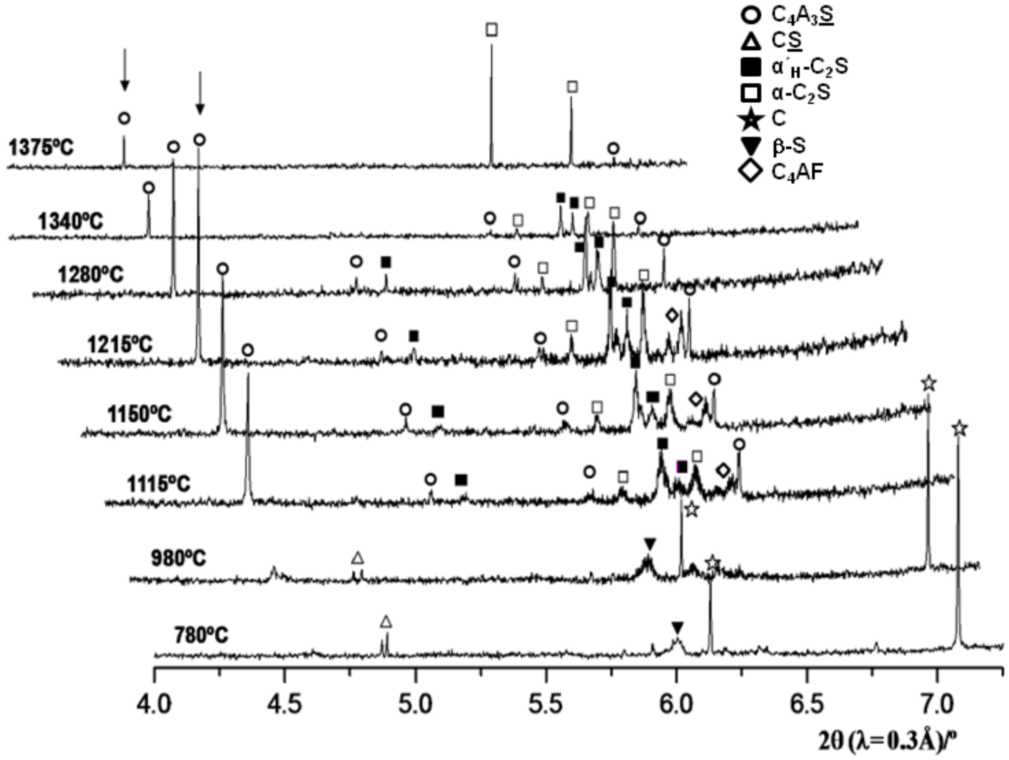

Figure 1.4. High-Temperature Synchrotron X-Ray Powder Diffraction (HT-SXRPD) raw patterns of a CSAF clinker activated with boron (BCSAF) (Adapted from De la Torre et al. 2011a).

Due to the phase stability field of the ye'elimite phase at high temperature, the clinkering temperature of BCSAF is a key issue which affects the final phase assemblage. It has been demonstrated that at a certain temperature, the phase assemblage is closed to the targeted one (50 wt% of C_2S, 30 wt% of $C_4A_3\underline{S}$ and 20 wt% of C_4AF); for instance, at 1215ºC the mineralogical composition of the mixture was 49.1(5) wt% of C_2S, 28.1(5) wt% of $C_4A_3\underline{S}$ and 22.8(4) wt% of C_4AF determined by SXRPD in combination with the Rietveld method. The presence of minor elements such as alkaline oxide or boron in raw mixes will decrease clinkering temperatures, as well as melting points of all the phases. For instance, the addition of 2 wt% of B_2O_3 to the raw materials decreased the minimum clinkering temperature, from 1300ºC down to 1150ºC (De la Torre et al. 2011a,b). The thermal formation and stability of this phase have been studied (Ali et al. 1994; Puertas et al. 1995; De la Torre et al. 2011b; Li et al. 2014), using as a raw material reagent grade $CaCO_3$, $CaSO_4$ and Al_2O_3, thus mechanism of formation may be slightly different from that occurring when using calcite, kaolin and gypsum. Some calcium aluminates, mainly CA or $C_{12}A_7$ are formed as intermediate phases and finally they react with $C\underline{S}$ to form ye'elimite above 900ºC. At high temperatures, $C_4A_3\underline{S}$ melts/decomposes (marked with arrows in Figure 1.4). It is worth to highlighting the diminution of the absolute integrated intensities of ye'elimite diffraction peaks above 1300ºC due to melting and/or decomposition of this phase. In addition, Touzo (2013) have studied the coexistence of calcium sulphoaluminate and ferrite solid solution at 1325 °C. Iron contents up to 8.8 wt% were found in the $C_4A_3\underline{S}$ phase coexisting with melt and very iron-rich ferrite. And it was suggested that control of the Al/Fe ratio would be an important parameter in optimising sulphoaluminate clinker production. Because, at high overall iron contents, it is difficult to avoid the formation of excessive amounts of liquid at 1325 °C, the rather rapid development of a very fluid melt over a short range of temperatures, the formation of other iron bearing phases such as monocalcium ferrite in iron-rich compositions and progressive replacement with increasing iron content of $C_4A_3\underline{S}$ by $CaSO_4$ as sulfate-containing solid.

In addition, the used of foreign elements promotes the decrease of the polymorphic transformation temperatures. This effect is important for the stabilization of the high temperature forms of C_2S. The α'_H-$C_2S \rightarrow \alpha$-C_2S polymorphic transformation in BCSAF clinkers is decreased from ~1370ºC to ~1000ºC by adding 2.0 wt% of B_2O_3, and this effect is important for the stabilization of high temperature forms of C_2S. The addition of selected foreign elements produces the stabilization α'_H-C_2S

polymorph, which is more hydraulically active. Active BCSAF materials were successfully prepared in the laboratory (Cuberos et al. 2010; Aranda et al. 2011; Álvarez-Pinazo et al. 2012: Ma et al. 2014a). The main goal in these works, was the quantitative demonstration of α'_H-C_2S polymorph stabilization by borax addition to BCSAF clinkers, and that this polymorph hydrates much faster than β-C_2S polymorph. Figure 1.5. shows both Rietveld plots of (a) BCSAF without any activator added and (b) BCSAF with 2.0 wt% of B_2O_3 added as borax. This figure also includes Rietveld quantitative phase analyses, showing that the activation was achieved as BCSAF with 2.0 wt% of B_2O_3 only contained α'_H-C_2S polymorph. Moreover, Álvarez-Pinazo et al. (2014) reported an in-situ synchrotron X-ray powder diffraction study for the first hours of hydration of these materials. Recently (Wesselsky and Jensen, 2009; Morin et al. 2011; Cuesta et al. 2012) highlighted that the effectiveness of addition of B_2O_3 with no other co-dopants for stabilizing α'-forms is poor, thus it is mandatory to add selected additional foreign elements such as sodium.

A recent study (Bullerjahn et al. 2014) has proved that iron-rich CSA contains ye'elimite with significant amounts of iron stabilizing the cubic form and enhancing its hydration rates. Moreover, they stated that ternesite ($C_5S_2\underline{S}$) was formed at certain clinkering conditions and it was found to be hydraulically active.

On the other hand, stoichiometric $C_4A_3\underline{S}$ is orthorhombic at room temperature (RT) (Calos et al. 1995; Cuesta et al. 2013). However, it forms solid solution with Na^+, B^{3+}, Si^{4+} and/or Fe^{3+}, among others, that seems to restore the cubic symmetry (Saalfeld and Depmeier 1972; Cuesta et al. 2014c). BCSAF clinker without activation presents a mixture of both polymorphs, meanwhile the activation promoted the stabilization of the cubic form, asterisk in Figure 1.5.

ACSA cements, with 20-30 wt% of $C_4A_3\underline{S}$, have also been investigated with the same aim of enhancing final performances of clinkers. However, this clinker preparation seems difficult because the optimum temperatures for the synthesis of alite and ye'elimite differ considerably. While C_3S needs at least 1350ºC to be formed and the reaction between free lime and C_2S is promoted by the apparition of melting phases (De la Torre et al. 2007), ye'elimite phase decomposition takes place above 1350ºC. However, the coexistence of both phases at temperatures between 1250 and 1300°C is possible by adding of a small amount of CaF_2 to raw mixture (Li et al. 2007b; Yanjun et al. 2007). Other authors have prepared ACSA clinkers by jointly adding fluorite and other minor elements such as Mg, Ba, Cu, Ti, Mn or Zn (Liu and Li 2005; Lingchao et al. 2005; Ma et al. 2006; Liu et al. 2009; Lili et al. 2009; Pérez-Bravo et al. 2014) Such clinkers exhibit a significantly improved grindability when compared to OPC clinker, although mechanical strengths strongly depend on the amount of added gypsum.

Cement Porsal was an attempt to produce a BCSAA cement (Viswanathan et al. 1978; Wolter 2005) with C_2S and $C_4A_3\underline{S}$ as main phases, and CA and $C_{12}A_7$ as secondary phases, combining their features. However, there is not information concerning the large scale production of Porsal. On the other hand, some laboratory studies state the feasibility of the production of this type of material (Pliego-Cuervo and Glasser 1979; Valenti et al. 2007; Martín-Sedeño et al. 2010) at low temperatures with the suitable phase assemblage and even using aluminum-rich waste materials for cost reduction.

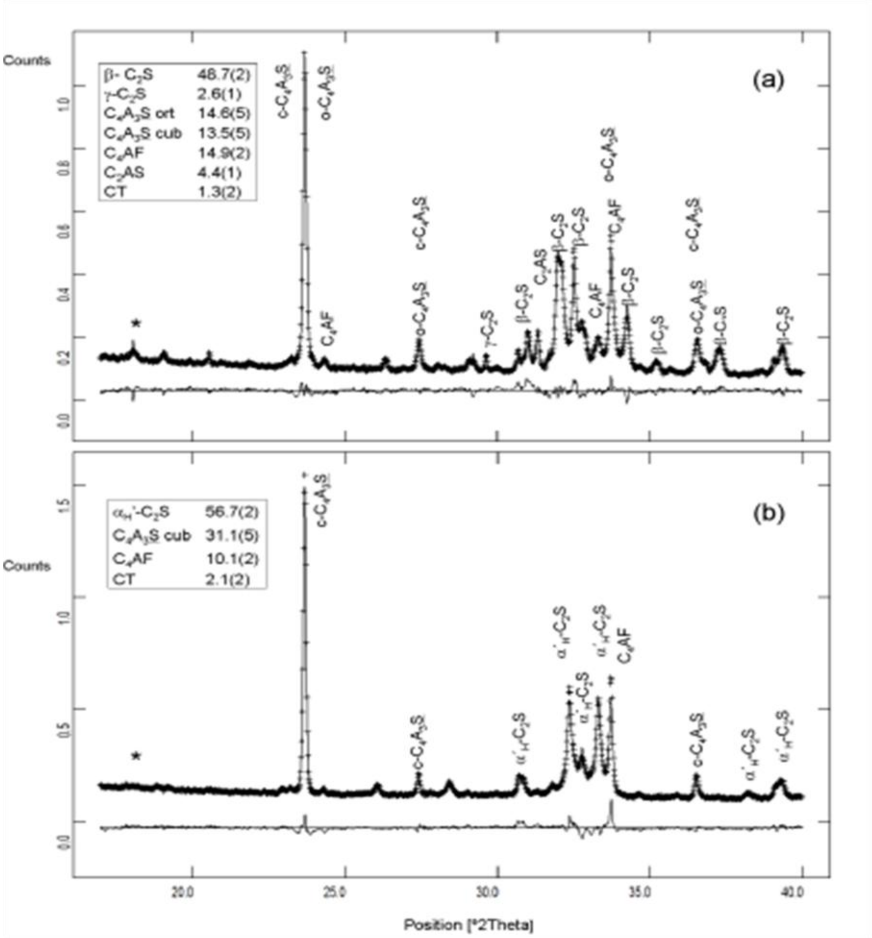

Figure 1.5. Rietveld plots of (a) BCSAF without any activator added and (b) BCSAF with 2.0 wt% of B_2O_3 added as borax (Adapted from Álvarez-Pinazo et al. 2012).

1.2.4. Commercial ye'elimite-containing cements

Nowadays, there are some commercial ye'elimite-containing clinkers/cements being produced and used for special applications in Europe, i.e. S.A.cement from Buzzi-Unicem, ALIPRE® 2009 from Italcementi Group, or CSA cement (model number 62.5, 72.5, 82.5, 92.5) from Tangshan Polar Bear Building Materials, China, among others.

CSA clinkers are mixed with different types of calcium sulphate carriers (gypsum, bassanite or anhydrite) and they are also commonly blended with OPC. Final performances highly depend on the amount of each component (Marchi and Costa 2011) yielding a variety of materials with applications such as Portland accelerator, fast-setting mortars, low-shrinkage and expansive mortars and concretes. Some results have been published about the use of this binder in concrete technology (Buzzi et al. 2011). This particular concrete exhibited rapid strength development, good resistance to freeze-thaw and excellent resistance to sulphate attack; however the durability under carbonation is still under investigation.

An industrial trial of low energy belite based cements in which BCSA cement was included was reported by Popescu et al. (2003), highlighting environmental profits of belite rich materials and even concluded that BCSA developed higher mechanical strengths than OPC at very large hydration ages. Although mechanical strengths at early ages were much lower than those of a typical OPC because this BCSA contained only ~12 wt% of $C_4A_3\underline{S}$.

Recently, BCSAF cements are emerging with the aim to substitute OPC. An industrial trial to producing around 2500 tons of BCSAF was carried out in early 2011 by Lafarge under the AETHER^{TM} project (http://www.aether-cement.eu/) (Walenta and Comparet 2011). Clinkering in a Portland industrial kiln was proven with lower operating temperatures (1225-1300ºC), reducing of CO_2 emissions by 25-30% in comparison with CEM (I) type OPC cement. Temperature in the clinkering zone was a key parameter as too high temperatures may give kiln blockage; loss of grindability and $C_4A_3\underline{S}$ decomposition with high SO_2 emissions and too low temperatures gave under burnt binder with high free lime and $C_{12}A_7$ contents. However, optimum clinkering temperature resulted in NO_x emissions being much lower than those of OPC fabrication (due to the lower burning temperature), and SO_2 measured industrial emissions at the same level than for OPC production. Moreover, the main technological disadvantage of these cements is related to their low very-early age's mechanical strengths because the hydration of belite is rather slow. However, this problem is being overcome by the activation of belite and high amounts of ye'elimite (Gartner and Li 2006; Cuberos et al. 2010; Morin et al. 2011). The production of active BCSAF cements involves the stabilization of highly reactive C_2S polymorphs, i.e. β-modified form and α-forms, as they react faster with water. Belite-activated BCSAF, **aBCSAF**, cements also have been patented by Lafarge (Gartner and Li 2006) with ~20-30 wt% of Klein's salt and α-forms of belite, due to addition of minor elements, such as B_2O_3 and Na_2O added as borax or P_2O_5, among others. These minor elements promote the stabilization of α'-forms of belite and the distortion of β-form. **aBCSAF** with 2.0 wt% of borax developed comparable mechanical strengths to those of OPC. Moreover, the industrial trial also includes the production of 2500 tons of this **aBCSAF** cements. This material develops mechanical strengths of 25 MPa at one day and the strengths seem to be even higher than those developed by type I 52.5 OPC after 7 days (Walenta and Comparet 2011). A second industrial trial (2011) has also been successful.

We would like to highlight that the compositional variability is much larger for CSA than for BCSAF clinkers (Aranda and De la Torre 2013). For example, CSA based materials contain from ~ 50 wt% to more than 70 wt% of ye'elimite and from negligible up to ~ 30 wt% of belite, meanwhile the laboratory-prepared aBCSAF clinker (De la Torre et al., 2011a,b) contains ~55 wt% of C_2S and ~30 wt% of $C_4A_3\underline{S}$.

Sokol et al. (2014) have very recently reported natural ye'elimite-larnite rocks found in the Hatrurim formation of the Negev Desert, Israel, which mineralogical compositions are similar to that of belite calcium sulphoaluminate cement clinkers.

Their mineralogy consists on 35-50 wt% β-C_2S, 15-20 wt% $C_4A_3\underline{S}$, 7-15 wt% ferrites, and 15–20 wt% fluorapatite and/or fluorellestadite. This study concludes that chalky and/or marly sediments with randomly distributed clay, phosphorite, and gypsum may be utilized as cheap naturally homogenized and pulverized mixtures for industrial production of BCSA cement clinker.

To finish this section, we would like to summarize and clarify the expected uses of ye'elimite containing cements. CSA cements (with prices ranging 250-350 €/ton of clinker) are being used for special applications but they are not intended to replace OPC (with prices close to 100 €/ton of clinker). Moreover, the high-demand of aluminum needed for CSA and BCSAA clinker fabrications makes these cements inappropriate for replacing OPC for large-scale inexpensive applications. However, the relatively lower aluminum content of belite-active BCSAF, ~15 wt%, coupled to the much lower CO_2 emissions (approximately 30-35% reduction) and higher gypsum-demand (close to 10 wt%) make BCSAF a potential alternative to OPC with expected prices only slightly larger than those of OPC cements. Concern remains related bauxite cost and scarcity, as remarked by Scrivener and Kirkpatrick (2008), Schneider et al. (2011) and Juenger et al. (2011) and also more studies about long term durability issues are needed.

1.2.5. Hydration of CSA cements

Hydration of cements can be summarized as a process of dissolution and crystallization of different phases. This is described in detail below.

The first step is the wetting of the cement; as soon as the water is added to the cement; both ye'elimite and the sulphate source (gypsum, bassanite and/or anhydrite) start to be dissolved. Only part of this exothermic process is usually recorded in a calorimeter owing to the time required for the mixing procedure and stabilization time, point (1) in Figure 1.6. Immediately after wetting, the following reaction takes place:

$$C_4A_3\underline{S} + 2\ C\underline{S}H_x + (38\text{-}2x)\ H \rightarrow C_6A\underline{S}_3H_{32} + 2\ AH_3 \qquad [1.3]$$

reaction [1.3] corresponds to the formation of ettringite ($C_6A\underline{S}_3H_{32}$), also known as AFt, and amorphous gibbsite (AH_3) by the reaction of $C_4A_3\underline{S}$ with soluble calcium sulphate(s) and water. Formation of ettringite will continue while calcium sulphate is present, signal (2) in Figure 1.6. Once the sulphate source is depleted and there is enough free water available, monosulphate also known as AFm ($C_4A\underline{S}H_{12}$) is formed (Winnefeld and Lothenbach 2010) according to equation [1.4].

$$C_4A_3\underline{S} + (16+x)\ H \rightarrow C_4A\underline{S}H\ (10+x) + 2\ AH_3 \qquad x=0,\ 2,\ 4 \qquad [1.4]$$

This is also an exothermic reaction which takes place once calcium sulphate is consumed, signal (3) in Figure 1.6. (Odler 2000). These two reactions ([1.3] and [1.4]) may take place in the early hydration of CSA and BCSAF cements. This is shown in Figure 1.7. where cryo-scanning electron microscopy micrographs of BCSAF pastes are shown. Pastes from BCSAF cements with 20 wt% of gypsum (Figure 1.7.a) showed a lot of acicular-hexagonal AFt crystals even at very early hydration ages, reaction [1.3]. Conversely, pastes from BCSAF cements with (only) 5 wt% of gypsum (Figure 1.7.b) showed, in addition to AFt crystals, thin-layered AFm crystals, due to reaction [1.4].

Very recently Hargis (2014) studied hydration of CSA cement in presence of gypsum, calcite and vaterite, and observed that calcite and vaterite reacted with monosulphoaluminate to give monocarboaluminate and ettringite (being vaterite more reactive), increasing the compressive strength. The presence of gypsum lowered the reactivity of both carbonates and unfortunately decreased the compressive strength values.

The influence of the polymorphism of $C_4A_3\underline{S}$ on hydration has been studied by Cuesta et al. (2014a). These authors observed that in the absence of additional sulphate sources, stoichiometric-ye'elimite (orthorhombic) reacts slower than doped-ye'elimite (cubic), and AFm-type phases are the main hydrated crystalline phases, as expected. Moreover, doped-ye'elimite produces higher amounts of ettringite than stoichiometric-ye'elimite. However, in the presence of additional sulphates, stoichiometric-ye'elimite reacts faster than doped-ye'elimite.

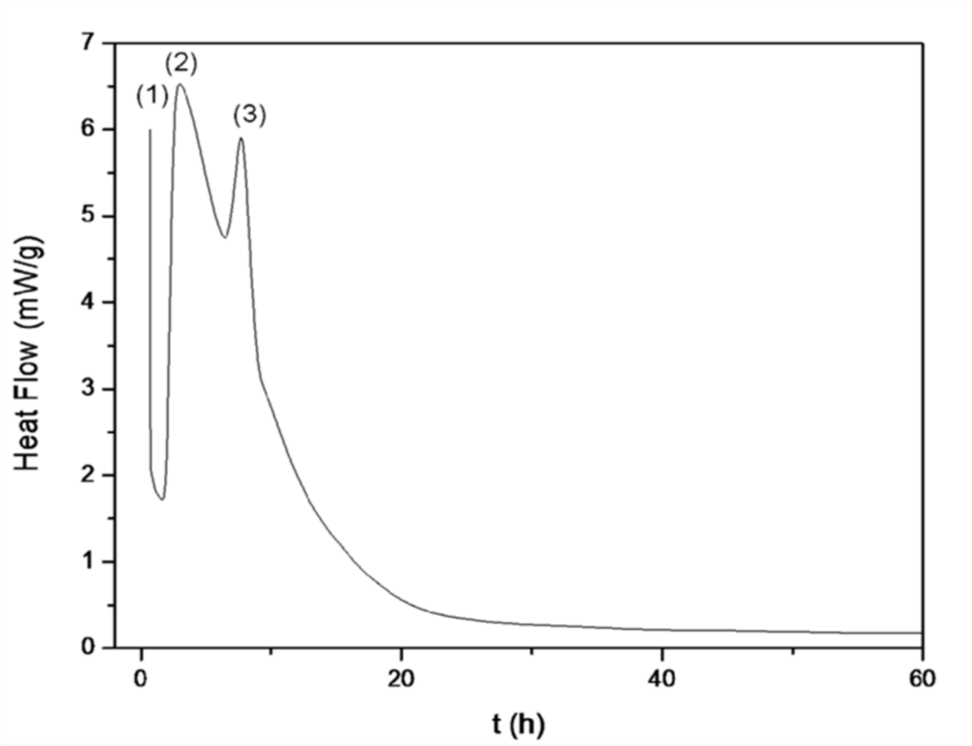

Figure 1.6. Calorimetry result of a BCSAF.

The most important reactions of most common minor phases are detailed below. Minor phases also react with water or calcium sulphate and somewhat contribute to rapid hardening, according to the following reactions (Bessy 1938; Meller et al. 2004).

$$C_4AF + 3\ C\underline{S}H_2 + 30\ H \rightarrow C_6A\underline{S}_3H_{32} + FH_3 + CH \qquad [1.5]$$

$$C_{12}A_7 + 12\ C\underline{S}H_2 + 113\ H \rightarrow 4\ C_6A\underline{S}_3H_{32} + 3\ AH_3 \qquad [1.6]$$

$$3\ CA + 3\ C\underline{S}H_2 + 32\ H \rightarrow C_6A\underline{S}_3H_{32} + 2\ AH_3 \qquad [1.7]$$

Ettringite is yielded in these reactions during the first hours of hydration, thus signal (2) in Figure 1.6. is also due to the heat release by these reactions, if these minor phases are present. Depending on the availability of calcium sulphates again, there are other alternative reactions for the direct hydration of these phases:

$$C_4AF + 16\ H \rightarrow 2\ C_2(A_{0.5}F_{0.5})H_8 \qquad [1.8]$$

$$C_{12}A_7 + 51\ H \rightarrow 6\ C_2AH_8 + AH_3 \qquad [1.9]$$

$$2\ CA + 11\ H \rightarrow C_2AH_8 + AH_3 \qquad [1.10]$$

Aluminum or iron hydroxides (AH_3 or FH_3) are initially amorphous phases as they cannot be directly detected by X-Ray Powder Diffraction (XRPD), but its occurrence may be confirmed by DTA-TG techniques (Cuberos et al. 2010; Martín-Sedeño et al. 2010; Morin et al. 2011). Later, these aluminum rich amorphous phases may crystallize as gibbsite.

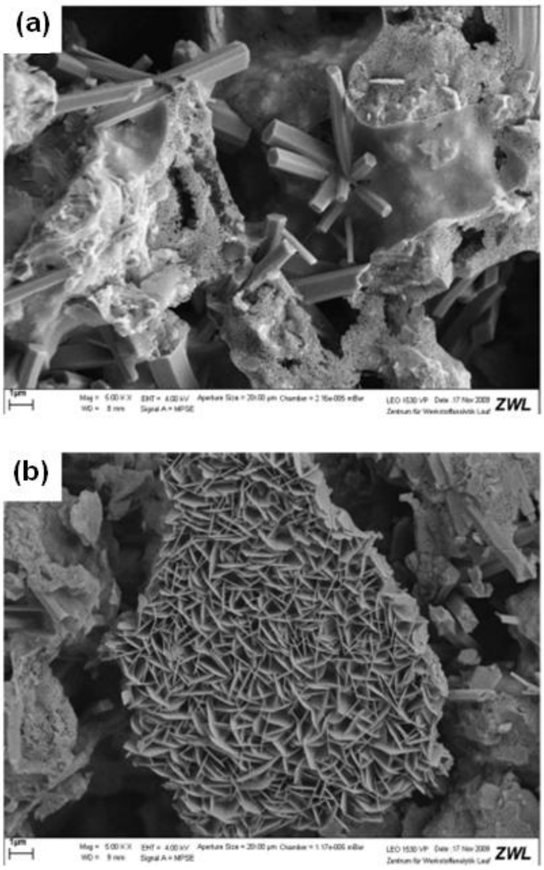

Figure 1.7. Cryo-SEM photographs of BCSAF cement pastes after 4 h of hydration for (a) 20 wt% of gypsum and (b) 5 wt% of gypsum (Cuberos et al. 2010).

The C_2S hydration is of special interest in BCSAF. The hydration reaction could be the same as that occurring in OPC independently of the rate of reaction of α- and β-polymorphs:

$$C_2S + (x+2-y)\,H \rightarrow C_ySH_x + (2-y)\,CH \qquad [1.11]$$

The hydration of belite to form the amorphous gel C_ySH_x and portlandite correspond to reaction [1.11]. However in BCSA pastes, belite coexists with aluminum rich amorphous hydrates and the formation of stratlingite is favoured

(Palou et al. 2005; Cuberos et al. 2010; Gartner and Macphee 2011; Álvarez-Pinazo et al. 2013):

$C_2S + AH_3 + 5\ H \rightarrow C_2ASH_8$ [1.12]

Reaction [1.12] consumes the amorphous AH_3 formed by the hydration reactions of aluminum-rich phases. The presence of stratlingite has been confirmed in BCSAF pastes by XRPD and DTA techniques by numerous independent investigations (Cuberos et al. 2010; Aranda et al. 2011; Morin et al. 2011; Álvarez-Pinazo et al. 2013), and play a role in the advance-ages mechanical strengths, and it is produced at a larger pace if high temperature polymorphs of belite are stabilized. The Figure 1.8. shows DTA signals of a BCSAF paste hydrated for 6 months (Morin et al. 2011). These data confirm the presence of CSH gel and the symbol # highlights the absence of the endothermic effect of AH_3 decomposition, being demonstrated that reaction [1.12] take place due to aluminum hydroxide disappearance.

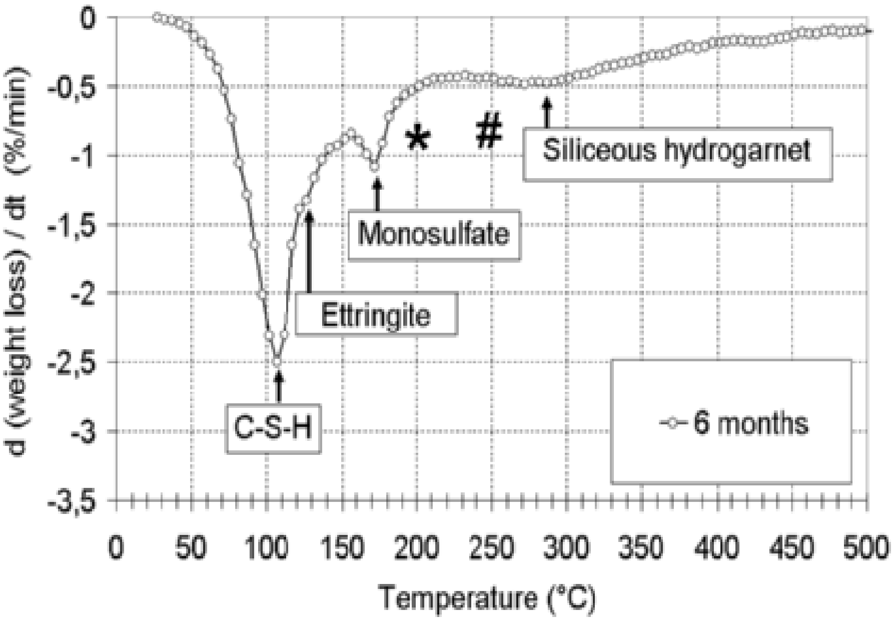

Figure 1.8. DTA result of a BCSAF (Adapted from Morin et al. 2011).

Other reactions need to be taken into account. Some studies have confirmed the presence of katoite phases, also known as siliceous hydrogarnet, Katoite has a structure related to the grossular or garnet, C_3AS_3, where some or all of the silicon is omitted and the charge being balanced by replacing each of the oxygen atoms to which it was attached by hydroxyl. Moreover, the Al^{3+} may be partly or wholly replaced by Fe^{3+}. Consequently the katoite solid solution, also known as hydrogarnet, may be expressed as $C_3A_{1-x}F_xS_{3-y/2}H_y$ (Taylor 1997), and can be formed according to chemical equation [1.13].

$$C_2S + 1/2\ C_4AF + 5\ H \rightarrow C_3(A,F)SH_4 + CH \qquad [1.13]$$

Reaction [1.13] justifies the formation of portlandite, which is not detected by XRD or DTA, through the consumption of ferrite. Consequently, this portlandite may be consumed by stratlingite as follows, producing larger quantities of katoite:

$$C_2ASH_8 + CH \rightarrow C_3ASH_4 \qquad [1.14]$$

Figure 1.8. shows the endothermic effect of siliceous hydrogarnet or katoite decomposition and the asterisk symbol is highlighting the absence of stratlingite after 6 months of hydration (Morin et al. 2011). Katoite formed by reaction [1.14] may be of interest for the durability of mortars and concretes based on BCSAF as portlandite is consumed. Finally, the effect of temperature on the hydration of CSA cements at very early ages has also been studied (Zhang and Glasser 2002).

The understanding of the hydration reactions are key for tailoring the properties of CSA and BCSAF mortars and concretes, but the microstructure development is also of the outmost importance. Very recently, the early hydration (less than 1 day) of three cementing materials (OPC, CSA and an blended OPC/CSA) was investigated in-situ by synchrotron x-ray tomographic microscopy (Gastaldi et al. 2011). The reaction kinetics and the morphological evolution of mineral phases of the three investigated cements was followed, and chiefly, it was possible to determine the three-dimensional evolution of the pore networks with a spatial resolution close to 1 µm.

The setting times of CSA and BCSAF cements (between 30 min and 4 h) are shorter than that for OPC and mainly depend on their ye'elimite content and the amount and reactivity of the added calcium sulphate (Zhang et al. 1999; Glasser and Zhang 2001; Li et al. 2007a; Marchi and Costa 2011). Furthermore, the setting time can be controlled with the use of retarders (Zhang and Glasser 2005) and also by the interaction with the filler (Pelletier-Chaignat et al. 2012).

All these issues depending on clinker composition, used of admixtures, amount and type of sulphate source, water to cement ratio, addition of additives or additions and so on. Hence, they are further studied in the following sections.

1.2.6. Role of sulphate source: type and content

As commented above, CSA and BCSAF cements are prepared by mixing the clinker with different amounts of a calcium sulphate set regulator such as gypsum, bassanite or anhydrite, or a mixture of them. Moreover, the amount and the reactivity of the added sulphate source (Pelletier-Chaignat et al. 2012; Glasser and Zhang 2001; Pera and Ambroise 2004; Telesca et al. 2014; Ioannou et al. 2014) play a key role in controlling the hydration of ye'elimite and the final performances of pastes/mortars/concretes.

The solubility and amount of the calcium sulphate source added to the clinker influences the ratio of formation of the main hydrate phases, i.e. AFt and AFm

(Sahu et al. 1991; Winnefeld and Barlag 2009; Winnefeld and Barlag 2010). On the one hand, increasing amounts of calcium sulphate provides with both calcium and sulphate ions necessary for the formation of high amounts of ettringite (see Figure 1.7.). This may lead to an expansive behaviour of the mixture due to the formation of AFt within the hardened matrix. This is of especial relevance when hydrating CSA, as these cements may contain very large amounts of $C_4A_3\underline{S}$ (Chen et al. 2012). On the other hand, low amounts of calcium sulphate promotes the formation of AFm phases, once sulphate ions have depleted (see Figure 1.7.), resulting in reduced fluidity and increased water demand and may lead to premature setting.

Other important issue is the type of calcium sulphate carrier added to CSA or BCSAF clinker: gypsum, bassanite or anhydrite. The setting behaviour can be controlled by the use of a reactive calcium sulphate like bassanite or gypsum which present quicker dissolution rate than anhydrite. In agreement with that, Álvarez-Pinazo (2014) published the very fast dissolution of bassanite with precipitation of gypsum, as well as the low dissolution rate of anhydrite and their consequents in BCSAF early hydration. Early strength properties are also enhanced by using gypsum (over anhydrite) as sulphate carrier (Péra et al. 2003; Pelletier-Chaignat et al. 2011; Berger et al. 2011a; Marchi and Costa, 2011). However, bassanite dissolves very fast and hence the initial setting time of the pastes and mortars is too short ~20 min to producing non-homogeneous samples with low compressive strength. In addition, low reactive calcium sulphate, such as some anhydrite, causes a lack of calcium and sulphate ions in the pore solution, leading to a delay in ettringite formation and strength development. Furthermore, CSA has also been used to improve the water resistance of plaster of Paris as it counteracts the high solubility of bassanite (Kuryatnyk et al. 2010).

Very recently was studied the hydration of two ye'elimite polymorphs (stoichiometric-ye'elimite (orthorhombic) and solid-solution-ye'elimite (cubic)) with and without presence of gypsum or anhydrite as additional sulphate sources (Cuesta et al. 2014a). In the presence of sulphate sources, the formation of AFm-type phases at late ages is avoided. The hydration in the presence of gypsum is accelerated when compared to the corresponding conditions without gypsum (mainly in stoichiometric ye'elimite) and as expected, the hydration of ye'elimite in the presence of anhydrite is very much slowed.

1.2.7. Role of water/cement ratio

The required w/c ratio in ye'elimite-containing cement pastes for full hydration is higher than for OPC which may yield pastes with larger pore diameters. For instance, a w/c ratio of 0.78 is needed for pure ye'elimite to fully react with the stoichiometric amount of anhydrite to yield ettringite (Winnefeld and Lothenbach 2010; Zhang and Glasser 2002; Bernardo et al. 2006). Moreover, both high and low w/c ratios may involve severe expansion (Chen et al. 2012); for the former, final strength development problems are also evolved (Ambroise et al. 2009). These undesirable properties (Chang et al. 2009) may be eliminated by using small particles (Chen et al. 2012) or additives. In addition, cements with very large amounts of ye'elimite may present shrinkage problems, and this effect is strongly correlated with porosity. In order to prevent water evaporation causing drying shrinkage, it is advisable to decrease the surface tension of water in paste pores, thereby lowering the capillary tension within the pore structure. As discussed above, CSA cements require larger amounts of water due to $C_4A_3\underline{S}$ hydration, thus evaporation of water is also facilitated. The use of some shrinkage-retardant admixtures will modify pore structure preventing the release of water (Ambroise et al. 2009).

The microstructure of pastes/mortars/concretes is affected by the water/cement (w/c) ratio that provides water to hydrate phases and the porosity (space) where hydration products can precipitate. CSA or BCSAF at low w/c ratio will develop a denser pore structure, being the space available for hydration products smaller. Moreover, this low water pastes can undergo self-desiccation, as ettringite formation requires huge amounts of water. This effect can be critical for expansion properties as large amounts of cement particles remain unhydrated after setting. This can cause expansion if cement is later exposed to external water from the environment, by the formation of secondary ettringite from the reactivity of anhydrous phases (Beretka et al. 1996). However, very dense frameworks difficult water diffusion to the interior of the mortars and concretes. High w/c ratio makes cements dimensionally stable, even with high amounts of ye'elimite; but the microstructure of the paste/mortars is more porous, which may result in lower mechanical strengths.

The w/c ratio affects the porosity of pastes. Low w/c ratios lead to low porosities, enhancing mechanical strengths, although in the first hours of hydration there is a loss of plasticity. High w/c ratios lead to highly porous microstructures which result in lower compressive strength values (Berteka et al. 1996; Bernardo et al. 2006; Marchi and Costa 2011). Reaction of ye'elimite and gypsum requires a theoretical water-to-binder mass ratio of 0.64. However this water-to-binder mass ratio will also depend on the minor phases as well as the final performances of the paste/mortar/concrete to be produced. Therefore, it should be underlined that very different w/c ratios have been used in the hydration reactions of CSA. These values range from quite low ratios 0.35-0.45, (Zivica 2000; Zivica 2001; Fu et al. 2003; Canonico et al. 2007) to quite large ones 0.70-0.80 (Winnefeld and Barlag 2009; Lura et al. 2010; Winnefeld and Lothenbach 2010; Winnefeld et al. 2011). However, the most used ratios range 0.5-0.6 (Bernardo et al. 2006; Valenti et al. 2007; Gastaldi et al. 2007; Alesiani et al. 2008; Telesca et al. 2011; Buzzi et al.

2011). Finally, there are studies varying this critical ratio. For instance, Chen et al. (2012) studied water-to-binder ratios of 0.30, 0.45 and 0.70.

In BCSAF cements the variability of the water-to-cement mass ratio is much smaller. Most studies use w/c=0.5 with more variability in the amount of sulphate carrier. For instance, w/c=0.5 and 10 wt% of $C\underline{S}$ was initially reported (Janotka et al. 2007; Adolfsson et al. 2007). Li et al. (2007a) used w/c=0.5, and 8 and 12 wt% of $C\underline{S}H_2$, for mortars and pastes, respectively. Morin et al. (2011) studied the hydration reactions of AETHER^{TM} using a w/c mass ratio of 0.5 with 5.3 wt% of $C\underline{S}$. Aranda (2011) also used a w/c ratio of 0.5 but adding 10 wt% of $C\underline{S}H_2$. Juenger and Chen (2011) used w/c=0.45 and variable amounts of sulphate carriers. Finally the effects of the amount of gypsum added to BCSA laboratory-prepared clinkers (β- or α_H-belite as main phase) with water to cement ratio 0.55 were also studied, being the optimum amount of gypsum close to 10 wt% (Álvarez-Pinazo et al. 2013).

1.2.8. Additions (Supplementary cementitious materials-SCMs)

First of all, we want to clarify the difference between additions and additives. Jackson (2004) according to standards defined additions as a material that is interground or blended in limited amounts into a hydraulic cement during manufacture either as a "processing addition" to aid in manufacturing and handling the cement or as a "functional addition" to modify the use properties of the finished product. However additives or admixtures are constituents which are added to improve the manufacture or the properties of the cement, e.g. grinding aids. The total quantity of additives should not exceed 1 per cent by mass of the cement. If it does, the quantity shall be stated on the packaging and/or on the delivery note.

These additives shall not promote corrosion of the reinforcement or impair the properties of the cement or of the concrete or mortar made from the cement.

Hence, ye'elimite-containing cements have been used as additions in Portland cements since its existence. Klein, in 1966, patented type K cements which present expansive properties, which consists on OPC with CSA cement as addition. The fundamental behaviour of these cements is based on the following reaction:

$$C_4A_3\underline{S} + 8\ C\underline{S}H_2 + 6\ CH + 74\ H \rightarrow 3\ C_6A\underline{S}_3H_{32} \qquad [1.15]$$

The presence of portlandite, released to the system mainly by C_3S hydration (from the OPC), makes the reaction pathway [1.15] more favourable than [1.3]. Consequently, three moles of ettringite are producing instead of one per each unit of $C_4A_3\underline{S}$, which result in a large potential for expansion (Kurdowski and Thiel 1981). Moreover, crystal size of ettringite is also affected by the presence of portlandite in the hydrating environment. In fact, ettringite crystals coming from reaction [1.15] are significantly smaller than those produced by the hydration of ye'elimite with gypsum, reaction [1.3], causing a different microstructure of the hydrating paste (Mehta 1973; Gastaldi et al. 2011).

At the same time CSA/OPC (80/20 mass ratio) blended with limestone filler and superplasticizer were studied for self levelling-applications and glass-fibre-reinforced composites (Pera and Ambroise 2004). Moreover, CSA has also been used to improve the strength of high-grade slag cement composed of granulated blast furnace slag, OPC and anhydrite. The only studied parameter was the gypsum amount which led to different hydrates (Michel et al. 2011). In addition, BCSAF cement performances may also be enhanced by its blending with OPC (Janotka and Krajci 1999; Janotka et al. 2003; Pelletier et al. 2010; Pelletier et al. 2011). BCSAF cements may present very short initial setting times, however, by blending with 15 wt% of OPC setting time is sufficiently enlarged for mortar-making technological procedures. Moreover, mortars with this blending develop higher mechanical strengths than (non-activated) BCSAF mortars.

Moreover from the point of view of sustainability, the use of by-product materials in the cement and concrete industry does have significant environmental benefits for reducing the negative impact of the cement industry. The incorporation of additions, such as blast furnace slag or pulverized fly ash, also known as supplementary cementitious materials (SCMs) (Lothenbach et al. 2011; Gartner and Macphee 2011; Snellings et al. 2012; Ma et al. 2014a; Ioannou et al. 2014), to partly replace CSA and BCSAF cements gives up a huge spectrum of blended cements that have been noted not only for its properties of reducing energy consumption and CO_2 emission (RECCE) but also for its environmental and economic benefits due to the valorisation of a “useless” product.

Furthermore, the addition of SCMs to cement may give the possibility of the modification of their properties (Quian et al. 2008), such as decreased hydration heat, improved workability of fresh mortar/concrete mix, improved chemical resistance, ultimate strength increase, and improvement of other engineering properties of concrete (Zivica et al. 2000).

However, the extent of replacement is limited by the following problems: reduced early strength, limited amounts of reactive SCMs and limited replacement by non-reactive SCMs without compromising final strength. In any case, it is essential to control/understand the hydration process (Winnefeld and Lothenbach 2010; Klaus et al. 2013; Le Saoût et al. 2013) without or with SCMs. The effect of the addition of by-products to OPC pastes has already been well described in the literature (Termkhajornkit et al. 2006; De Weerdt et al. 2011). However, for CSA and

BCSAF cements, it is still needed to understand all parameters involved in the cement-SCMs hydration, and the key roles of water and SCMs contents.

We can highlight two works about blending ye'elimite-containing cements with mineral admixtures like fly ash, silica fume, and blast furnace slag to study pozzolanic reactions (Zivica 2000; Zivica 2001). Unfortunately, the water-to-cement mass ratio used was quite small (ranging between 0.32 and 0.41), hence, full hydration of the pastes did not take place. The beneficial effects of limestone filler with calcium sulphoaluminate cement have been reported (Pelletier-Chaignat et al. 2012). The hydration reactions have been studied for a fixed w/c mass ratio of 0.8, but two $C\underline{S}H_2$/CSA mass ratios (0.19 and 0.40) and two temperatures (5 and 20ºC) were tested. The compressive strengths were higher for limestone than for the same level of substitution with inert filler (quartz in this study). In addition, very recently, the potential use of a bioethanol by-product called high lignin residue (HLR) for SCM production was examined (Ataie and Riding 2014). Pre-treated CSA and high lignin residue ash (HLRA) increased the early reactivity of cement paste when used as 20% replacement of cement in the system whereas unpretreated CSA was found to severely suppress the hydration reaction. The highest compressive strength was obtained for samples containing HLRA.

There is also a situation where the waste to be safely disposed within concrete may also help as an addition which influences the hydration reaction. Municipal solid wastes were blended with CSA and the compressive strength, pore structure, hydration phases, and leaching behaviour of Zn and Pb were characterized (Qian et al., 2008). Recently, municipal solid waste incineration fly ash was successfully used as a raw material to prepare calcium sulphoaluminate cement in the laboratory. Compressive strength, durability and microstructure of the prepared CSA cement-based materials were studied (Guo et al. 2014).

1.2.9. Uses of CSA cements to stabilize wastes

OPC blended cements containing high amounts of blast furnace slag or pulverized fly ash are usually used to encapsulate intermediate-level and low-level radioactive wastes. Unfortunately, the high alkalinity of these systems may lead to high corrosion rates with reactive metals within such wastes releasing hydrogen and forming expansive corrosion products. According to that problem with OPC, blended CSA cements are being tested as alternative encapsulation binders mainly due to their highly dense matrixes and lower alkalinities (Zhou et al. 2006). Hayes and Godfrey (2007) used Rockfast (commercial CSA) which theoretically would need 37 wt% of gypsum and 0.54 water-to-cement mass ratio for full hydration. These authors varied the water-to-binder mass ratio from 0.50 to 0.65, and different gypsum and pulverized fly ash contents with very encouraging results. Also, Cau Dit Coumes et al. (2009) have tested OPC/CSA blended cements since the setting time is shortened which is useful for nuclear waste encapsulation.

Finally, CSA cements have been also investigated to solidify and stabilize different types of wastes: i) wastes containing large amounts of soluble zinc chloride which is a strong inhibitor of OPC cement hydration (Berger et al. 2011b,c); ii) galvanic sludge with high amounts of chromium which was stabilized in blended CSA-bottom ash cement (Luz et al. 2006; Luz et al. 2009); and iii) heavy metals in general, such as Cr, Pb, Zn, Cd (Peysson et al. 2005). In this sense, the valorisation of phosphogypsum (a side-product in the fabrication process of phosphoric acid) as binder for CSA has been also studied (Kuryatnyk et al. 2008).

1.2.10. Additives or admixtures

As commented above additives or admixtures are materials other than hydraulic cements, water or aggregates that are added immediately before or during mixing.

They are materials such as grinding aids, retarders, superplasticizers, and so on (Jackson 2004).

The workability and mechanical properties of mortars and concrete are affected by the addition of additives such as water-reducing substances (superplasticizers), air-entraining agents (Uchikawa 1995), accelerate or retard setting or hardening, and so on. The workability of cement pastes is a performance index representing how easily it is mixed or transported, and also showing the ability of filling voids, and it is related with homogeneity (Palacios et al. 2009). Its control helps to improve strength and other hardened properties. Additives are adsorbed by particles and favour their dispersion; hence, their use has become a common practice in cements due to lower w/c contents, within a limited range, which is related with higher mechanical strength values (Björnstrom and Chandra 2003).

A water reducing agent does not substantially modify the degree of hydration (α); if α increases or decreases at early ages, it should be termed as accelerating or retarding water reducer, respectively. Superplasticizers improve the workability of concrete by introducing electrostatic, steric and/or electrosteric repulsion and causing deflocculation. These mechanisms are explained by their molecular structure and adsorption characteristics (Zhang et al. 2002). That repulsion depends on the type and amount of additive (Palacios et al. 2009), cements powder composition, gypsum and alkalis content, specific particle surface, particle size distribution and type of mineral additions. This effect can be measured through the rheological behaviour of the pastes and mortars (Banfill 2006).

There are several types of superplasticizers (Laźniewska-Piekarczyk 2014): i) First-generation superplasticizers were primarily derived from natural organic materials such as sugars and lignins (extracted from wood pulp). These products had some limitations and produce retard when overdosed; ii) Second-generation superplasticizers are derived from petroleum feed stocks: sulphonated naphthalene or melamine condensates with formaldehyde. These products offer greater water reduction and are less detrimental when overdosed; iii) Third generations are polycarboxylates (PC), which are copolymers synthesized from carefully selected monomers. They often provide about 20 min of effectiveness before the concrete exhibits significant slump loss. However, this can be modified by a re-dosage.

In addition, there are a wide variety of retarders used in oil well cementing to control the setting time of the cement. The time that the cement is required to be flowable and pumpable into the well varies depending on the well size, temperature, pressure and the location (depth) within the well to which the cement is to be placed. The use of retarders and accelerators in cement slurries is often essential to be adapted to those conditions demanded by the well (Pang et al. 2014). Examples of different retarders include organic phosphonates, phosphates, borates, saccharides, and lignosulphonates, to name a few. Retardation consists of two effects (Cheung et al. 2011): the increase in the induction period, and the reduction of hydration rate after hydration accelerates. The different kinds of retarders are often observed to display quite different mechanisms for retarding cement slurries. The mechanisms of set retardation fall into four regimes (Cheung et al. 2011; Bishop and Barron 2006): (i) calcium complexation preventing precipitation of some phases, (ii) formation of a semipermeable layer later broken down by osmotic pressure gradients, (iii) surface adsorption of retarders directly on anhydrous surface, and (iv) nucleation and growth poisoning of hydrates. The first two are now generally considered unlikely; the first one because very strong chelaters can be moderate retarders while strong retarders can be moderate chelaters (Thomas and Birchall 1983) and the second one due to direct SEM observations (Juilland et al. 2010).

The special mechanism of "dissolution-precipitation" proposed by Bishop et al. (2003) for organic phosphonic acids would appear to be a special case of the third mechanism (surface adsorption of retarders directly on anhydrous surface). They affirm that the mechanism by which the phosphonic acid inhibits cement hydration consists on two steps: First, dissolution, whereby calcium is extracted from the surface of the cement grains, exposing the aluminum-rich surface to enhanced hydration; second, precipitation, whereby the soluble calcium phosphonate oligomerizes either in solution or on the hydrate surface to form an insoluble polymeric Ca phosphonate. The Ca phosphonate binds to the surface of the cement grains, inhibiting further hydration by acting as a diffusion barrier to water as well as a nucleation inhibitor (Bishop et al. 2003).

On the other hand accelerators are used to produce shotcrete. Chemically, accelerating admixtures for concrete can be divided into four major groups (Prudêncio 1998): alkaline silicates, alkaline earth metal carbonates/hydroxides, sodium and potassium aluminates, and alkali-free accelerators often based on aluminium sulphate or calcium sulphoaluminate. A side effect of the traditional alkali-rich accelerators is a significant reduction of the ultimate strength (typical values for strength reduction at 28 days range between 20% and 50%) (Prudêncio 1998). Wieland et al. (2014) used an accelerator, which is free of alkalis and contains aluminium sulphate and formate as the main components. Previous studies showed that the addition of an accelerator gives rise to a significant increase in the amount of ettringite formed (Paglia et al. 2001 and Xu and Stark 2005). Furthermore, both pH and sulphate concentration were found to decrease while calcium and aluminium concentrations increased in the pore solution (Xu and Stark 2005). In summary, the accelerator is expected to exert an effect on the mineral composition of the cement paste and consequently on the pore water conditions.

The selection of the type and content of the additive is essential to achieve the desired final properties (porosity, strength, and so on). This can be optimized through rheological studies of cement pastes, mortars and concretes at early ages. This will be explained in detail in Sections 1.2.11 and 1.3.1.

Ambroise (2009) studied three types of polyether polyol added to CSA pastes and mortars. The results show that polyol reduces drying shrinkage of CSA-based mortars without affecting the nature of hydrates formed, the effect of polyol mainly depends on its molecular weight and the presence of polyether increases the quantity of ettringite in hydrated pastes and modifies the morphology of ettringite, leading to the formation of hollow crystals. In addition, Ma (2014b) presented an experimental study on the effects of polycarboxylate superplasticizer on the setting time and the mechanical performance of BCSA cements to solve the problems of quick set at early stage. The results indicate that the presence of the superplasticizer can delay the initial setting time remarkably when the dosage reaches 0.075% and mortars presented lower strengths at early stage, but higher at 28 days, when this additive was used.

1.2.11. Rheological properties of mortars and concretes

The rheological properties are essentials in the structural characterization process of the particle-liquid system, and in the evaluation of the particle-particle interactions in the paste. The control of the rheological behaviour allows the improvement of the homogeneity, obtaining flowless samples which will affect in the most important final performances of materials, as mechanical strengths. Moreover, the paste dispersion state influences in the properties of the corresponding mortars and concretes (Hanehara and Yamada 2008).

Rheology of fresh cement is often characterized by its workability. In the case of the first hydration hour(s) of ye'elimite-containing systems is very important as large amounts of ettringite (needles shape particles) are formed and plasticity and both workability strongly depend on the rate of this reaction. There are few studies concerning the improvement of the workability of CSA cements. The addition of selected additives enhance the workability of these pastes, hence dispersing CSA particles and slowing down the hydration rate enlarging the setting time (Chang et al. 2009). Moreover, CSA pastes with additives such as water-reducing substances (superplasticizers) may present excellent dispersion at low w/c ratios and, consequently, improved mechanical performances.

To continue this section, it would be remarked that it is well known in concrete and mortar technology that the grading of aggregate is one of the main factors influencing the hardened concrete strength (Neville 1995; Metha and Monteiro 2006). Aggregate is added to cement paste for various reasons: aggregate is cheaper than cement and it confers to concrete higher strength and better durability than cement paste. In a first approach, it is widely admitted that adding as much as possible aggregate to the cement paste is desirable in order to produce better concretes. However, the rheological properties of a suspension (viscosity, yield stress, and so on) are increasing functions of the volume fraction occupied by the particles (Chong et al. 1971; Coussot 2005; Stickel and Powell 2005). Adding particles to a paste also reduces its workability; consequently it is necessary to reduce this effect in order to design concrete and mortar mixtures containing the maximum amount of solid particles as possible that can be transported, placed and finished easily. Mixtures of particles of different size give less porous packing than mixtures of particles of the same size. Moreover the particle size distribution that provides the highest packing density also gives the most flowable suspensions when the particle volume fraction is prescribed. This is why mixtures of particles of different size have been used in concrete technology for a long time in order to produce granular packing of maximal compacity (Roussel 2012). The packing density of dry particle mixtures is also of interest in many other industrial fields (ceramic, pharmacy, civil engineering, food, etc.) and the properties of dry particle mixtures have attracted the interest of mathematicians, physicists and engineers for a long time.

1.2.12. Durability of CSA concretes

Ye'elimite-containing cements and their corresponding mortars and concretes are considered as durable binders. Nevertheless, degradation processes should be taken into account, depending on the environment on which these mortars or concretes are serving. There are different ways of cement degradation e.g. carbonation, sulphate attack or chlorine diffusion. All these effects need ions diffusion through the porous microstructure. In CSA and BCSAF cements, the resistance to diffusion is enhanced due to the quick water consumption during the hydration process. Moreover, porosity decreases during hydration due to the large amount of hydration products generated at very early ages (Bernardo et al. 2006). Quillin (2001) reported a durability study with two commercial CSA cements (w/c ratio of 0.56) and within the characterization-techniques included carbonation (and accelerated carbonation), sulphate resistance, chloride ingress, compressive strengths and expansion measurements. In comparison with OPC concretes, these showed excellent sulphate resistance and slightly higher carbonation rates.

Atmospheric carbon dioxide can react with hydration products by dissolution in the pore solution of the pastes, and so increasing CO_3^{2-} ion concentration. This phenomenon will cause three effects: i) lowering pH value, ii) precipitation of $CaCO_3$ by the reaction of carbonate ions with Ca^{2+} ions and iii) possible damaging of ettringite. Porosity/w/c ratio determines the degree of resistance to carbonation. Carbonation appears to be more rapid in CSA than in Portland concretes, leading to partial decomposition of ettringite, which may cause a moderate strength loss (Sharp et al. 1999; Mechling et al. 2013). Zhang and Glasser (2005) reported a study about two Chinese CSA concretes: i) a normal strength concrete sample from a crane column made during the cold winter of 1982 with hot mix water with w/c=0.55-0.60 and by adding 1 wt% of $NaNO_2$ as anti-freeze; and ii) a high-strength concrete sample from a pile made in summer 1993 with w/c~0.3 and by adding unstated superplasticizer and retarder. The normal strength concrete was carbonated in a comparable rate to OPC concretes and ettringite persisted after more than twenty years of service. In addition, decreasing w/c ratio (high-strength concrete) increases resistance to carbonation as there was not free water available to dissolve CO_2. These result are in agreement with Mechling (2013) who reported that when the w/c ratio is low CSA cement has mechanical strength and resistance to carbonation quite comparable to those of Portland cement, with a far superior dimensional stability, most especially in a natural environment; and Mechling (2013) proposed as a solution, to mix CSA cement with Portland cement as new environment-friendly cement. Summarizing up, if low w/c ratios are employed carbonation is not an important problem for CSA concretes (Zhang and Glasser 2005; Mechling et al. 2013); but, carbonation studies are lacking for aBCSAF pastes/concretes.

Other problem of durability is the expansion of concrete during hydration because the sulphate diffusion into mortar matrixes may cause expansion due to delay of ettringite formation (Chen et al. 2012). Bizzozero et al. (2014) found that there is a critical amount of gypsum leading to unstable expansion and failure of the samples in calcium aluminate and sulphoaluminate systems. However, after some days of hydration water may be exhausted and, unless there is another deterioration mechanism (as leaching) (Berger et al. 2011d), the expansion due to the delayed formation of ettringite is not significant (Glasser and Zhang, 2001). Moreover, due to the absence of C_3A in the phase assemblage of BCSAF cements, they seem to be excellent sulphate resistant binders.

1.3. Physical properties

1.3.1. Rheological behaviour

Rheology is the science that studies the flow and deformation of the matter under the influence of a mechanical force. It is concerned particularly with the material behaviour which cannot be described by the simple linear models of hydrodynamics and elasticity. Some of these departures are due to the presence of colloidal particles or to the influence of surfaces of the matter (IUPAC). The resistance of a fluid to flow may be considered in terms of the situation existing between two parallel planes, one of which is moving in its own plane relative to the other. It is assumed that flow is confined to the single direction thus defined, and that the velocity varies linearly with distance in the direction perpendicular to the planes (Schramm 1984; Moreno 2005).

The control of the rheological behaviour of cement pastes is a key point (Champenois et al. 2013; Tattersall and Banfill 1993) to improve the workability of mortars (Banfill 2006) and to obtain more homogeneous mixtures and hence, improved mechanical properties in general and compressive strengths in particular. In addition, the setting evolution of cement pastes can be also followed at very early hydration times by following their viscosity values.

1.3.2. Compressive strength

The compressive strength is defined as the capacity of a material or structure to withstand loads tending to reduce size. It can be measured in a testing machine by checking the deformation of the material by applying pressure. At their compressive strength limit, some materials fracture and others deform irreversibly. So a given amount of deformation may be considered as the limit for compressive load. Compressive strength is a key value in the design of structures. In cement based materials (mortars) high values of compressive strength are desired. According to standard UNE-EN 197-1=2011 there are two types of compressive strengths: i) nominal compressive strength, which is the compressive strength at 28 days of hydration, determined in accordance with the standard UNE-EN 196-1, and it must achieve the value required for each type of cement; and ii) initial compressive strength, which is the compressive strength at 2 or 7 days of hydration, determined in accordance with the standard UNE-EN 196-1, and it must also achieve the value required for each type of cement.

Factors determining (Taylor 1997) the compressive strength of a cement paste include: i) characteristics of the cement, such as clinker composition and microstructure, gypsum content and particle size distribution; ii) w/c ratio and contents of air and of any admixtures present in the mix; iii) mixing conditions; iv) curing conditions (temperature and relative humidity); v) curing age; vi) the manner of testing, including the water content of the specimen. The factors listed determine the degree of hydration of the clinker phases and the phase composition and microstructure of the hardened paste, which in turn determine its physical properties, including strength.

1.3.3. Shrinkage/Expansion properties (Length Changes)

The expansion (or shrinkage) experienced in mortars is mainly related to the nature of the pore structure, which affects the mobility of ions and the available space to accommodate new phases. Both adequate deformability and strength values are required to allow expansion without the formation of cracks.

OPC pastes slightly expand during wet curing; a small shrinkage, called autogenous shrinkage, occurs during sealed curing (Taylor 1997). The origin of expansion is associated with ettringite formation and there are two head theories: the “crystal growth” and “swelling”. First one concludes that expansion is caused by the growth of ettringite crystals and the related crystallization pressure (Bentur and Ish-Shalom 1974; Ogawa and Roy 1981; Herrick et al. 1992; Deng and Tang 1994); but according to the last theory (Mehta 1973, 1975, 1982), the expansion is due to the adsorption of water molecules on ettringite, resulting in interparticle repulsion and swelling.

Expansion is enhanced or depressed by a relatively high or low nucleation rate, respectively. Calcium, sulphate or hydroxyl ions i) promote, when present in elevated amounts, the formation of fine ettringite crystals on the surface of $C_4A_3\underline{S}$ particles or ii) combine, if their concentration is relatively low, with enough $Al(OH)_4^-$ ions to produce large ettringite crystals in the bulk solution. The importance of hydration studies on CSA-based cements aimed at investigating the pore solution chemistry was highlighted (Andac et al. 1999; Winnefeld and Lothenbach 2010).

In conclusion, ye'elimite-containing cements, if hydrated in a strong alkaline environment (Wang et al. 1986; Telesca et al. 2014), in the presence of lime or with a considerable amount of added calcium sulphate, are potentially expansive;

on the contrary, they tend to attain a dimensional stability when hydrated, at not elevated pH values or in the absence of lime, together with relatively moderate calcium sulphate additions. Recently studies stated that CSA expansion was reduced by presence of calcite and vaterite, irrespective of the presence of gypsum (Hargis et al. 2014). Moreover high amounts of ye'elimite have been related to high expansion values, because sulphate diffusion into mortars matrixes may cause expansion due to delay of ettringite formation. Sulphate ions may diffuse and react with calcium ions yielding gypsum precipitation. However, this gypsum requires unreacted ye'elimite and water to produce ettringite, and the later is the limiting reactant. Therefore, ye'elimite-based mortars expand (Janotka et al. 2007) more than OPC mortars (~0.25 and -0.10%, respectively), hence commercial ye'elimite-based cements have been used for shrinkage compensating concrete (Chen et al. 2012).

1.3.4. Setting

The setting and hardening of cement is a continuous process, but two points are distinguished for test purposes:

i) The initial setting time, which is the interval between the mixing of the cement with water and the time when the mix has lost plasticity, stiffening to a certain degree. It marks roughly the end of the period when the wet mix can be moulded into shape. It is determined by monitoring the repeated penetration of a needle into a fresh cement paste of standard consistence (using the Vicat apparatus), and the time of initial setting is taken when the distance between the needle and the base plate is of 6±3 mm according to UNE-EN 196-3.

ii) The final setting time, which is the point at which the set cement has acquired a sufficient firmness to resist a certain defined pressure and according to UNE-EN

196-3 corresponds to a penetration of the needle of only 0.5 mm in the cement paste specimen.

There are several parameters which affects initial and final setting times such as water/solid ratio, fineness, sulphate source, solubility and so on. For example Pelletier-Chaignat (2012) measured the setting times of samples containing calcium sulphoaluminate clinker and gypsum combined with quartz filler or limestone filler. The results show that the use of limestone filler instead of quartz filler accelerates the early hydration of the cement, thus shortening the initial setting time.

1.4. Crystallochemistry of main phases of ye'elimite-containing cements

In this section, the crystallography of the main cement phases present in CSA-based cements will be described, where ye'elimite and belite are the two major anhydrous phases.

i) *Ye'elimite, also named Klein´s salt or tetracalcium trialuminate sulphate, [$Ca_4A_{l6}O_{12}(SO_4)$, $C_4A_3\underline{S}$].*

Ye'elimite is the major mineralogical compound in CSA cements. And it is liable for high mechanical strengths at early hydration ages.

Stoichiometric calcium sulfoaluminate or ye'elimite, can be described as a sodalite ($M_4[T_6O_{12}]X$) where M=Ca, T=Al, and X=SO_4, and crystallizes as a tectoaluminosilicate sodalite structure (Cuesta et al. 2013). This structure was first analyzed by Hanstead and Moore (1962) using X-ray powder diffraction, Wang et al. (1990) and Saalfeld and Depmeier (1972) reported atomic parameters for a cubic crystal structure with space group I-43m and a=9.195 Å. In 1995, Calos published an orthorhombic crystal structure, Pcc2 space group, which has been revised by joint neutron and X-ray powder diffraction Rietveld refinement and atomistic calculations (Cuesta et al. 2013). Recently, the disordered crystal structure of cubic stoichiometric ye'elimite at 800ºC has been satisfactorily studied in the I-43m space group using a split-atom model (Kurokawa et al. 2014). The Klein´s salt published crystallographic data are shown in Table 1.4. Fe-Si-doped ye'elimite is pseudo-cubic at room temperature with a phase transition on heating (Cuesta et al. 2014c).

Table 1.4. Klein´s salt polymorphs crystallographic data.

Polymorph	**Space Group**	**Unit cell parameters**				**V/Z**	**Ref.**	
		a (Å)	**b (Å)**	**C (Å)**	**β (º)**	**(Å^3)**	**bibl.**	**ICSD**
Cubic	I-43m	9.205	9.205	9.205	90.0	390	(a)	9560
Orthorhombic	Pcc2	13.028	13.037	9.161	90.0	389	(b)	80361
Tetragonal	P-4c2	13.031	13.031	9.163	90.0	389	(c)	-
Cubic	I-43m	9.197	9.197	9.197	90.0	389	(d)	-
Orthorhombic	Pcc2	13.036	13.035	9.168	90.0	346	(e)	-
Cubic at 1073 K	I-43m	9.253	9.253	9.253	90.0	396	(d)	-
Cubic at 1073 K	I-43m	9.248	9.248	9.248	90.0	396	(d)	-
Cubic at 1073 K	I-43m	9.243	9.243	9.243	90.0	395	(f)	-

(a) Saalfeld y Depmeier 1972; (b) Calos et al. 1995; (c) Zhang et al. 1992; (d) Cuesta et al. 2014c; (e) Cuesta et al. 2013; (f) Kurokawa et al. 2014.

Figure 1.9. shows two simulated diffractograms of two of the $C_4A_3\underline{S}$ polymorphs (orthorhombic and pseudo-cubic). As seen in this figure, all the peaks of the pseudo-cubic structure are also present in the orthorhombic form. We highlight that

the RT pseudo-cubic form is not a strict ye'elimite polymorph as it required the presence of dopants with in the crystal structure.

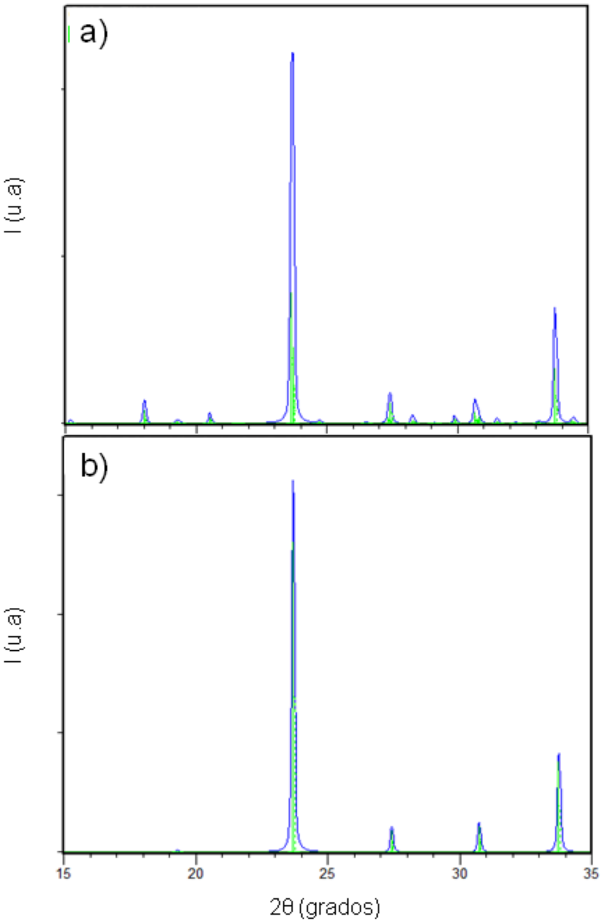

Figure 1.9. Region 15 ° to 35 ° (2 θ) of the theoretical diffractograms. (a) Stoichiometric (orthorhombic) $C_4A_3\underline{S}$ (Cuesta el al. 2013); (b) Doped (cubic) $C_4A_3\underline{S}$ (Cuesta el al. 2014c).

i) *Belite or dicalcium silicate [Ca_2SiO_4, C_2S].*

Belite is of great interest in BCSAA and BCSAF cements as it is the main component with a weight percentage of about 60 wt%. Belite may present five stoichiometric forms (Mumme et al. 1996) γ, β, α'_L, α'_H and α, on heating, with β-C_2S being the form that commonly prevails in OPC and in BCSAF and BCSAA without activation as it is stabilised by elements substitution(s). The structures of all are built from Ca^{2+} and SiO_4^{4-} ions. The arrangements of these ions are closely similar in the α, α'_H, α'_L and β polymorphs, but that in γ-C_2S is somewhat different. γ-C_2S is much less dense than the others polymorphs. Polymorphic transformations in function of temperature are shown in Figure 1.10. Physical and chemical properties of phases can be altered by introducing defects or strains in crystalline structures. Moreover, these defects can even stabilize high-temperature forms of C_2S at room temperature (Ghosh et al. 1979; Nettleship et al. 1992). The different type of defects can be produced by the addition of foreign elements to form solid solutions (Jelenic et al. 1978) or by specific thermal treatments (Fukuda and Ito 1999). There are many studies concerning the chemical-stabilization of β-C_2S by foreign ions such as SO_3, B_2O_3, Cr_2O_3 Na_2O, K_2O, BaO, MnO_2 and Al_2O_3 (Pritts and Daugherty 1976; Kantro and Weise 1979; Matkovic et al. 1981; Fierens and Tirlocq 1983; Ziemer et al. 1984; Benarchid et al. 2004; Cuesta et al. 2014b).

These investigations concluded that the hydration reactivity of stabilized β-C_2S depends on preparation parameters that influence particle and crystallite size. These parameters include temperature, type and amount of stabilizer, and fineness of the final ground product. The stabilization of α'-forms by introduction of foreign oxides, such as MgO, P_2O_5, K_2O, BaO, Na_2O, B_2O and SO_3 has also been studied (Bensted 1979; Fukuda et al. 2001; Park 2001; Cuesta et al. 2012). These works stated that hydraulic properties were increased when compared to the materials without foreign ions. The stabilization of α'-belite forms in a cement matrix can be attained by introducing minor elements, such as alkaline oxide, boron or phosphor, in raw materials (Morsli et al. 2007a,b; Li et al. 2007a; Wesselsky and Jensen 2009; Cuberos et al. 2010; Morin et al. 2011).

Table 1.5. shows the crystallographic information of the corresponding belite polymorphs. The crystal structures of the α'$_H$, α'$_L$ and β are derived from that α form by progressive decreases in symmetry, which arise from changes in the orientations of the SiO_4^{4-} tetrahedral and small movements of Ca^{2+} ions (Taylor 1997). Such structures belong to the family of the glaserite, $K_3Na(SO_4)_2$ (Moore 1973). However, the γ-C2S framework belong to the olivine type structure (O'Daniel and Tescheischwili 1942).

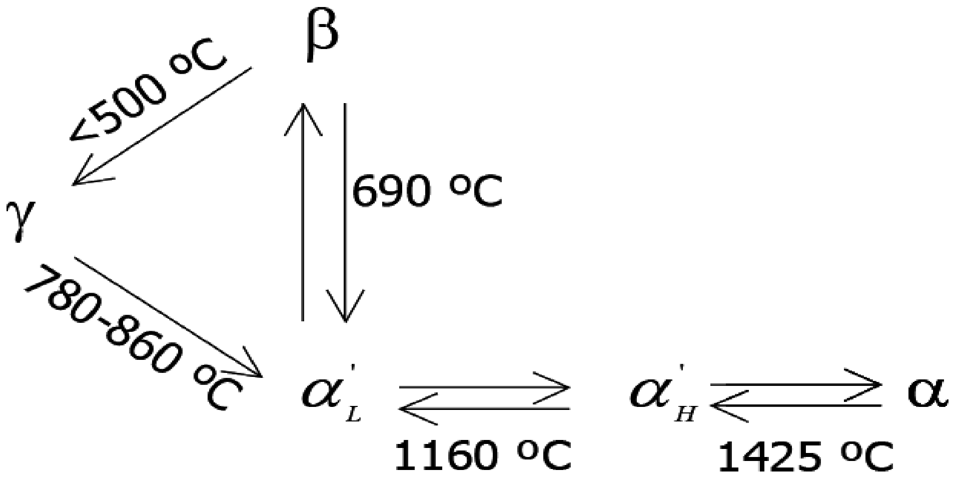

Figura 1.10. Belite polymorphic transformations with temperature.

Figure 1.11. shows the simulated diffractograms of different C_2S polymorphs. The presence of ions in the structure stabilizes the high temperature forms at RT. The stabilization of the high temperature polymorph is due to both ionic substitutions and quenching. The existence of α and α′$_H$ clinker has been also published (Regourd and Guinier 1974).

Generally belite clinker may contain between 4 and 6 wt% of substituent oxides, usually Al_2O_3 and Fe_2O_3. Relations between the percentage of oxides in the clinker and in the belite were published. SO_3 content in belite (Sb) is connected with the SO_3 present in the clinker (Sc) thought the following equation: Sb = 1.23Sc + 0.24, Sb was also calculated from the clinker SO_3 content, excluding soluble sulphates (Sc), according to: Sb = 3.36Sc +0.55 (Hall and Scrivener 1998). It has been noted that the limit K_2O dilution in belite is around 1.2 wt% (Chan et al. 1988).

Table 5.2. Belite polymorphs crystallographic data.

Polymorph	**Space group**	**Unit cell parameters**				**V/Z**	**T(ºC)/**	
		a (Å)	**b (Å)**	**c (Å)**	**β(º)**	**(Å^3)**	**Stabilized**	**ICSD**
α	$P6_3/mmc$[a]	5.420	5.420	7.027	90.0	89.4	-	81099
	$P6_3/mmc$[b]	5.532(9)	5.532(9)	7.327(11)	90.0	97.1	1545/-	82998
	P-3m1[b]	5.532(9)	5.532(9)	7.327(11)	90.0	97.1	1545/-	82999
α'$_H$	Pnma[a]	6.7673(4)	5.5191(4)	9.3031(6)	90.0	86.9	-/5% (molar) $Ca_3(PO_4)_2$	81097
	Pnma[b]	6.871(0)	5.601(0)	9.556(1)	90.0	92.0	1250/-	82997
	Pmnb[c]	5.647(1)	7.037(1)	9.644(2)	90.0	95.8	-/$Ca_{1.8}Sr_{0.2}SiO_4$	49662
	Pnma[d]	6.8263(3)	5.4684(3)	9.2658(4)	90.0	86.5	RT/ B_2O_3 and Na_2O	-
α'$_L$	$Pna2_1$[b]	20.527(2)	9.496(1)	5.590(1)	90.0	90.8	1060/-	82996
	$Pna2_1$[e]	20.863(2)	9.5000(8)	5.6005(5)	90.0	92.5	-/ $Ca_{0.84}Sr_{1.16}SiO_4$	39203
	$P2_1cn$[f]	5.566	9.355	20.569	90.0	89.3	-	39100
β	$P2_1/n$[a]	5.512(0)	6.758(0)	9.314(0)	94.6	86.5	-/0.5% (en peso) Cr_2O_3	81096
	$P2_1/n$[g]	5.48(2)	6.76(2)	9.28(2)	85.5	85.7	-	24640
	$P2_1/n$[h]	5.502(1)	6.745(1)	9.297(1)	94.6	86.0	-	963
	$P2_1/n$[i]	5.5127(1)	6.7586(1)	9.3266(2)	94.5	86.6	RT/Al_2O_3	-
γ	Pbnm[a]	5.082(0)	11.224(0)	6.764(0)	90.0	96.5	-	81095
	Pbnm[j]	5.081(2)	11.224(5)	6.778(10)	90.0	96.6	-	200707

(a) Mumme et al. 1995; (b) Mumme et al. 1996; (c) Catti et al. 1984; (d) Cuesta et al. 2012; (e) Il´inets and Bikbau 1990; (f) Udagawa et al. 1979; (g) Midgley 1952; (h) Jost et al. 1977 ; (i) Cuesta et al 2014b; (j) Udagawa et al. 1980.

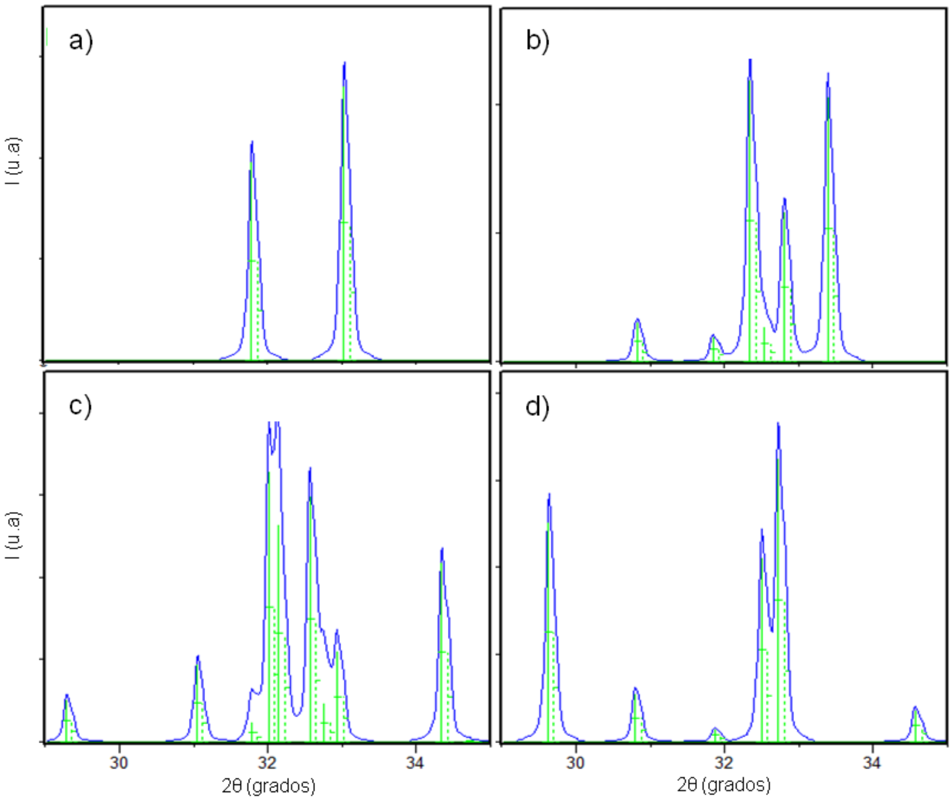

Figure 1.11. Range from 29 to 35º (2θ) of the theoretical diffractograms. (a) α-C_2S at RT (Mumme et al. 1995), (b) α'$_H$-C_2S at RT (Cuesta et al. 2012), (c) β-C_2S at RT (Mumme et al. 1995) y (d) γ-C_2S at RT (Udagawa et al. 1980).

To finish this section crystallochemistry of main hydrated CSA cement phases will also be described.

ii) *Ettringite or AFt phase.*

AFt (Al_2O_3-Fe_2O_3-tri) is calcium sulphoaluminate hydrate and have the general formula $[Ca_3(Al,Fe)(OH)_6.12H_2O]_2X_3xH_2O$, where x is, normally at least, ≤ 2 and X represents one formula unit of a doubly charged, or with reservations, two formula units of a singly charged anion. The term AFt refers to the three units of CX in an alternative way of writing the formula, $C_3(A,F)\cdot 3CX\cdot yH_2O$ [or

$C_6(A,F)X_3 \cdot yH_2O]$, where y = x + 30. In case of ettringite, the anion X = SO_4^{2-}. The crystal structure can be described as a compact columns of $[Ca_3Al(OH)_6.24H_2O]^{3+}$ composition, running parallel to the prism (c axis), with the X anions and, usually, H_2O molecules in the intervening channels. Figure 1.12 shows ettringite crystal structure.

i) *AFm phases*

AFm (Al_2O_3-Fe_2O_3-mono) phases have a layer structure with the general formula $[Ca_2Al(OH)_6]X \cdot xH_2O$ where X denotes one formula unit of a singly charged anion, (for instance OH^- or $[SiAlO_2(OH)_4]^-$ in the case of stratlingite, or half a formula unit of a doubly charged anion (for instance SO_4^{2-}) placed in the interlayer space jointly with water molecules. The compounds crystallize in hexagonal planes. The presence of AFm-phases with different layer spacings is justified twofold: i) by the partial anion replacement OH^-/SO_4^{2-} within the layers; and ii) by the progressive release of the water molecules as a consequence of the hydration of other phases. Stratlingite (Rinaldi et al. 1990), kuzelite (Allmann 1977) or C_2AH_8 are AFm-type phases and are formed when the sulphate source (gypsum, bassanite or anhydrite) is depleted and there is enough free water available (Winnefeld and Lothenbach 2010). There are other AFm-type phases such as monocarbonates (François et al. 1998) or monochlorides (Renaudin et al. 1999) that used to appear in chemically aggressive environments.

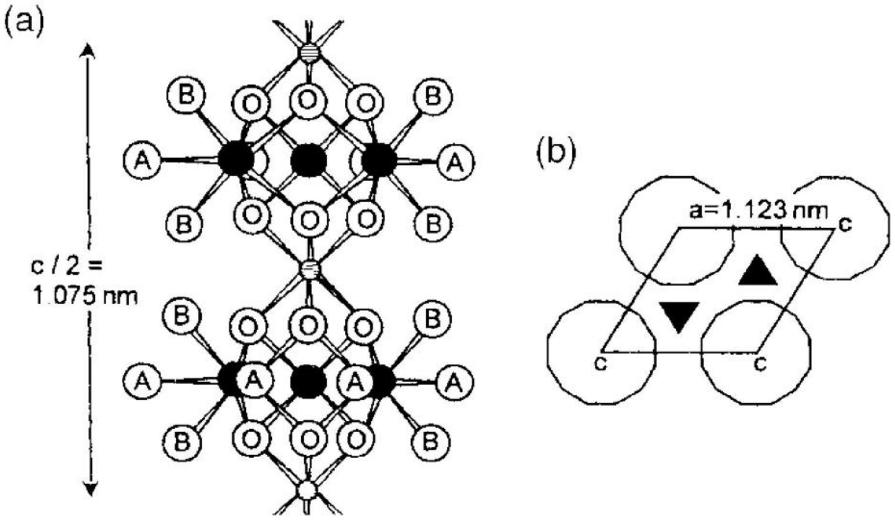

Figure 1.12. Crystal structure of ettringite. a) Composition of the columns, filled circles=Ca^{2+} ; striped circles = Al^{3+}; open circles: O = OH groups, A and B = H_2O. b) Triangles represent the locations of the SO_4^{2-} in the spaces between columns (Barnes and Bensted 2002).

1.5. Methodologies

In the present work, different techniques were used. The most important will be discussed next.

1.5.1. Laboratory X-Ray Powder diffraction (LXRPD) and Rietveld method

Powder diffraction patterns, are obtained by the interaction of X-rays (or neutrons or electrons) with crystalline compounds. Crystalline compounds have long range periodic order. The position, height and even width of these reflections may be used to determine many aspects of the sample structure/microstructure. Two most recent books in 'Powder Diffraction' have been published by Pecharsky and

Zavalij (2005) and Dinnebier and Billinge (2008). Hugo Rietveld in late sixties (Rietveld 1967; Rietveld 1969) devised "The Rietveld method" which is a technique for a deeper characterisation of polycrystalline compounds by treating in a 'better/different' way the powder diffraction patterns.

That supposed a conceptual breakthrough due to the very original contribution of the Rietveld method to powder diffraction: 'To use measured powder pattern intensities instead of reflection (peak) intensities'. This breakthrough, together with the coming of new technologies (computers), allowed to properly dealing with strongly overlapping reflections. The introduction of this technique was a key step forward in the analysis of crystalline powder patterns, because since to that moment the information was extracted from reflection intensities which were a very serious difficulty in the case of overlapping reflections.

Originally the Rietveld method was devised for the refinement of crystal and magnetic structures from powder neutron data. However, today the uses of the Rietveld method are numerous and help extracting the maximum information already present in a powder diffraction pattern. This information is listed just below and it must be highlighted that the Rietveld method is making a profound impact in every listed use as it increases the accuracy and precision of the extracted results. It can also be said that Hugo Rietveld did not envisage some of these uses including quantitative phase analysis (Rietveld 2010). From the position of the diffraction peaks: i) lattice parameters, ii) space group determination, iii) qualitative phase analysis (phase identification), and iv) macro-strain; from the intensities of the diffraction peaks: v) crystal (nuclear) structure (including atomic positions, occupation factors and atomic displacement parameters), vi) magnetic structure, vii) texture (preferred orientation), and viii) quantitative phase analysis; from the widths/shapes of the diffraction peaks: ix) micro-strains (mainly in solid solutions), and x) coherent diffraction domain size(s).

This Rietveld (whole-profile) method uses a least squares approach to optimise a theoretical line profile until it matches in the best possible way the measured sample powder diffraction profile (see equation [1.16]); where S_y is the function to be minimised, w_i is the statistical weight, and y_i(obs) and y_i(cal) are the observed and calculated powder diffraction intensities for the i-point of the powder pattern, respectively.

$$S_y = \sum_i w_i \, | y_i(\mathrm{obs}) - y_i(\mathrm{cal}) |^2 \qquad [1.16]$$

The calculated intensity, y_i(cal), for each point of the powder pattern, $2\theta_i$, is obtained as the sum of the contribution of all reflections (k) which give intensity to that i-point above the background, $y_b(2\theta_i)$, see equation [1.17]:

$$y_i(\mathrm{cal}) = y_b(2\theta_i) + S_\alpha \sum_k m_k \, |F_k|^2 \, h(2\theta_i - 2\theta_k) \, Lp(2\theta_i) \, P_k \qquad [1.17]$$

where S_α is the scale factor for the pure crystalline α-phase to be studied, k stands for the reflections which contribute to that point of the pattern, mk is the multiplicity of that reflection, F_k is the structure factor of that reflection, $h(2\theta_i - 2\theta_k)$ is the function that distributes the intensity of that reflection in a given 2θ range, $L^p(2\theta_i)$ stands for the Lorentz and polarization correction, and P_k stands for additional corrections that may be needed (preferred orientation, extinction, etc.).

Equation [1.17] may be extended to a sample containing m-crystalline phases, see equation [1.18], by summing up the contribution of every crystalline phase.

$$y_i(cal) = y_b(2\theta_i) + \sum_{i=1}^{m} S_i \sum_{k} m_k \left|F_k\right|^2 h(2\theta_i\text{-}2\theta_k)\ Lp(2\theta_i)\ P_k \qquad [1.18]$$

This method has several applications (above), however we will focus on the quantitative phase analysis.

1.5.1.1. Rietveld quantitative phase analysis (RQPA)

Several steps have to be fulfilled for a successful Rietveld quantitative phase analysis. First of all, sample has to be properly prepared and this will depend upon the nature of the sample itself and the diffractometer where the data will be taken. Secondly, the diffractometer should be well aligned and maintained. In modern diffractometers different optical configurations are possible and the optimal set-up should be used. Under these two pre-requisites, a good powder diffraction pattern may be collected and RQPA can be carried out. It must be highlighted that the results of any analysis cannot be better than the raw data. Therefore, in order not to spend/waste a lot of time in data analysis/evaluation without conclusive results a lot of care is needed in these two initial steps.

A third step follows once good powder diffraction data have been collected. Every crystalline phase in the sample should be identified. This is easy to say but sometimes quite complex to fulfil. The strong peak overlapping in the diffraction patterns does not allow to conclusively determining all phases present in some cases. Then a possible strategy follows, we compute the RQPA with the phases which are clearly present in the pattern and, from the net intensity in the difference curve, the remaining low-content phases are determined. Alternatively, a trial-and-error method can be used. In addition to the main, clearly-observed phases, dubious phases are added to the Rietveld calculation and its absence/presence can be individually estimated.

In any case, the fourth step is to carry out the RQPA with the appropriate software, when the main (all) phases are identified. In our case GSAS (Larson and Von Dreele 2000; Toby 2001) was the software package used and it´s one of the widest used software. Many other packages can also be used for RQPA and we underline just a few: FULLPROF, BGMN, SIROQUANT, TOPAS and HighScore Plus. In addition to the raw data, any Rietveld program needs a control file to execute the refinements. In this control file, the crystal structures of the different components must be included. The fit is carried out by optimising all appropriate variables such as: i) scale factor of every crystalline phase; ii) background parameters for the chosen function; iii) unit cell parameters for every crystalline phase; iv) peak shape parameters for every computed phase; and finally, v) correction parameters which may be phase-dependent (such as preferred orientation, extinction, etc.) or pattern-dependent (zero-shift, absorption correction when working in transmission geometry, etc.). Usually, for RQPA the structural descriptions (atomic positional parameters, atomic displacement parameters and occupation factors) are not optimised but kept as reported in the structural studies.

The RQPA method does not require calibration curve or internal standard. However, the crystal structures of all crystalline constituents must be known. This is a prerequisite as the process consists on the comparison between the measured and the calculated patterns (the calculated pattern being computed from the crystal structures).

Recently a chapter about Rietveld Quantitative Phase Analysis (RQPA) of OPC clinkers, cements and hydration products (Aranda et al. 2012; Aranda et al. 2015) has been issued. The application of RQPA to clinkers/cements/pastes is not an easy task for the following reasons: i) there are many phases, usually more than five, which increases the diffraction peak overlapping and so the correlations; ii) each phase has its own mass absorption coefficient which may yield the microabsorption problem; iii) the small mean penetration depth of X-rays (~30 μm for Cu Kα, 1.54 Å) implies that only a thin layer is analyzed in the Bragg-Brentano θ/2θ geometry which may lead to poor particle statistics; iv) some phases, for instance alite or gypsum crystallize as plaques which show preferred orientation and so increases the errors; v) phases can crystallize as several polymorphs that must be identified a priori; vi) the diffraction peak broadening for some phases may be anisotropic and it must be properly model; and vii) the atomic impurities inside each phase are not known and their scale factors are computed for ideal/stoichiometric phases. In any case, this method has several advantages over other methods based on powder diffraction and other technologies (microscopy, thermal analysis, etc.).

The direct output of the RQPA is a set of scale factors, one for every crystalline phase within the mixture with computed crystal structures. In addition, several other parameters may be of interest: i) unit cell parameters (to have an idea of the existence of solid solutions); ii) preferred orientation of some phases (to have an insight of the particle shapes of these phases); iii) peak shape widths to know about the microstructures. The key transformation of the phase scale factors to phase contents is discussed in a section below. However, it must be highlighted that the best available structural description should be used in order to extract the best possible scale factor value for every phase. This is evaluated by the flatness of the difference curve and also by obtaining low Rietveld-disagreement indices (R-factors). However, the lowest R-factors may also be obtained for wrong analyses. So, it is important to optimise those parameters that allow their minimization without excessive correlations.

As stated above, conventional RQPA requires all crystal structures to be known. Aranda et al (2012) reported the main hydrated and anhydrous cement standards phases. There are alternative whole-pattern quantitative phase analysis methods for crystalline phases with unknown structures (Smith et al. 1987; Taylor and Zhu 1992; Scarlett and Madsen 2006; Snellings et al. 2014).

The output of a RQPA study is a set of m-crystalline phase scale factors, $\sum_m S_\alpha$, for a sample with m-crystalline phases. A phase scale factor, S_α, is related to the phase weight content, W_α, by equation [1.19] (Hill and Howard 1987; Bish and Howard 1988):

$$S_\alpha = K_e \frac{W_\alpha}{\rho_\alpha \quad V_\alpha^2 \quad \mu_s} \qquad [1.19]$$

where K_e is a constant which depends on the diffractometer operation conditions, ρ_α is the crystallographic density of the α-phase, V_α is the unit cell volume of α-phase, and μ_s is the sample mass absorption coefficient. Equation [1.19] can be rewritten as given in equation [1.20]:

$$S_\alpha = K_e \frac{W_\alpha}{(ZMV)_\alpha \quad \mu_s} \qquad [1.20]$$

where instead of using ρ_α, the relation between S_α and W_α is based on the 'ZMV' term with Z being the number of chemical units/formulas within the unit cell, M being the molecular mass of the chemical formula, and V the unit cell volume. Once the crystal structure is known, the 'ZMV' term is known. In any case, the parameter to be extracted, W_α, depends on the phase scale factor, S_α, but also on K_e and μ_s. Unfortunately, these two variables are not known and they cannot be derived from the powder diffraction pattern of the sample under study.

Currently, there are three main ways to derive the phase content, W_α, from the Rietveld refined scale factor, S_α. These three methods are based on different mathematical approaches and they have different experimental complexities. They will be treated in detail just below (Gualtieri et al. 2014; Madsen et al. 2011):

i) Normalization to full crystalline phase content method. The simplest approach is the approximation that the sample is composed only of crystalline phases with known structures. These crystal structures are incorporated into the control file, and it was already shown (Hill and Howard 1987) that the weight fraction of α-phase, for a m-crystalline phase mixture, may be given by equation [1.21]:

$$W_\alpha = \frac{S_\alpha (ZMV)_\alpha}{\sum_{i=1}^{m} S_i (ZMV)_i} \qquad [1.21]$$

The use of equation [1.21] in RQPA eliminates the need to measure the instrument calibration constant, K_e, and the sample mass absorption coefficient, μ_s. However, the method normalizes the sum of the analysed weight fractions to 1.0. Thus, if the sample contains amorphous phases, and/or some amounts of unaccounted for crystalline phases, the analysed weight fractions will be overestimated.

This approach is by far the most widely used method in RQPA. However, it must be highlighted that the resulting weight fractions are only accurate if the amount of unaccounted crystalline phases and amorphous content are very small (negligible) which may be not the case in anhydrous cements and for sure is not the case in cement pastes.

ii) Internal standard method. A second, more experimentally-demanding, approach is to mix the sample with a crystalline standard in a known amount, W_{st} (also known as spiking method). This standard must be free of amorphous content or at least its non-diffracting content must be known. This (artificial) mixture must be homogenised as the particles should be randomly arranged. Under these considerations, equation [1.22] is fulfilled, where S_{st} is the Rietveld scale factor of the standard in the artificial mixture (Hill and Howard 1987):

$$W_\alpha = W_{st}\,\frac{S_\alpha (ZMV)_\alpha}{S_{st}(ZMV)_{st}} \qquad [1.22]$$

The addition of the standard dilutes the crystalline phases in the sample. This may be quite problematic for low-content phases. A procedure for Rietveld quantitative amorphous content analysis was outlined, in which the effects of systematic errors in the powder patterns were studied (De la Torre et al. 2001). The approach requires two powder patterns to be collected but it minimizes the errors. Firstly, a powder pattern of the sample of interest is collected and the crystalline phase contents are determined as stated in the previous section (normalised to a 100% of crystalline phases). A second pattern is collected for the sample mixed with the internal standard. The weight fraction added of the internal standard is known, W_{st}, as it was weighed. The RQPA gives an overestimated value of this content, R_{st}, due to the presence of amorphous phase(s), misfitting problems of the analysed crystalline phases, and because some crystalline phases may not be included in the control file due to several reasons (its crystal structure is not known, the phase was not identified, etc.). This overall content is hereinafter named ACn which stands for Amorphous and Crystalline not-quantified, to highlight that not only an amorphous fraction but any not-computed crystalline phase and any misfit problem (for instance the lack of an adequate structural description for a given phase) may contribute to this number. The method derives the (overall) ACn content of the sample from the small overestimation of an internal crystalline standard, equation [1.23] (De la Torre et al. 2001):

$$\text{ACn} = \frac{1 - W_{st} / R_{st}}{100 - W_{st}} \times 10^4 \text{ (wt \%)} \qquad [1.23]$$

For this second refinement, the phase ratios between the crystalline phases in the sample may be kept fixed to the values obtained in the first fit and only the fraction of the added standard is optimised. Under these conditions, the overall ACn content is derived and this is applied to the weight fractions determined in the first fit to place them in an absolute scale. The errors associated to this approach and the optimum amount of standard has been discussed (Westphal et al. 2009). Finally, NIST standard reference material (SRM) 676a, corundum (α-Al_2O_3) powder, has been certified to have a phase purity of 99.02% ± 1.11% (95% confidence interval) by RQPA against a suitable primary standard (powder silicon carefully prepared from a single crystal). This novel certification method permits quantification of amorphous content for any sample of interest by this spiking method (Cline et al. 2011). This methodology has been applied to anhydrous cement and also to pastes. However, the addition of an internal standard may alter the cement hydration reactions, dilutes the phases in the pastes, microabsortion problems, and so on.

iii) External standard method (G-factor approach). To avoid complications that may arise from mixing an internal standard with the sample, it is possible to use an external standard method. This approach requires the recording of two patterns in identical diffractometer configuration/conditions for Bragg-Brentano $\theta/2\theta$ reflection geometry. The method was proposed sometime ago (O'Connor and Raven 1988) and very recently applied to anhydrous cements (Jansen et al. 2011a) and organic mixtures (Schreyer et al. 2011). This method consists on determining the diffractometer constant, K_e, with an appropriate standard (for instance silicon powder from Si-single crystal), see equation [1.24], derived from equation [1.19]:

$$G = K_e = S_{st} \frac{\rho_{st} \; V_{st}^2 \; \mu_{st}}{W_{st}} \qquad [1.24]$$

where S_{st} is the Rietveld scale factor of the (external) standard, ρ_{st} corresponds to the density of the standard, V_{st} is the unit cell volume of the standard, W_{st} is the weight fraction of the standard (ideally 100 wt%) in the external standard pattern, and μ_{st} is the mass attenuation coefficient of the standard. This method is also known as G-method as the standard allows to calculate the G-factor of the diffractometer in the operating conditions.

The calculated G-factor represents a calibration factor for the whole experimental setup and comprises the diffractometer used, radiation, optics, and all data acquisition conditions, (for instance, detector configuration, integration time, etc.). This G-factor is used to determine the mass concentration of each phase of the sample under study using equation [1.25]:

$$W_\alpha = S_\alpha \frac{\rho_\alpha \; V_\alpha^2 \; \mu_s}{G} \qquad [1.25]$$

This method allows determining the absolute weight fractions by using a diffractometer constant that must be previously determined. However, the mass attenuation coefficient of the sample is needed, μ_s. This must be independently determined, and the most common way to obtain it, in cements, it is by X-ray fluorescence spectrometry (Jansen et al. 2011a). This methodology has been applied to anhydrous OPCs (Jansen et al. 2011a) and to OPC pastes (Jansen et al.

2011a,b) and Álvarez-Pinazo et al. (2013) in anhydrous and hydrated ye'elimite-based cement (BCSAF). From equation [1.25], it is clear that the weight fractions of all computed phases within the control file do not need to add up to 100 wt%. From the difference between 100 wt% and the sum of the crystalline phase contents, an overall unaccounted/left-out weight percentage, ACn, can be derived. In any case, the external standard method is experimentally more demanding but it may have the brightest future for the study of hydration reactions. This sentence is based on the lack of need of spiking an internal standard. The addition of an internal standard is a very important drawback in hydration reaction studies since not only dilutes the phases in the sample but it may also interfere with the hydration reactions.

Very recently Snellings (2014) have not identified amorphous content OPC using both external and internal standard methods. And also was reported that RQPA estimates using the G-factor method were inconsistent with those obtained with the Rietveld method combined with the internal standard method (Gualtieri et al. 2014). In particular, it should be assessed whether the approximation in the determination of the X-ray mass attenuation coefficient of the mixture, usually calculated from the chemical analysis, and its relationship to the actual powder packing coefficient, is a source of inaccuracy.

In addition LXRPD studies could be performed by two different geometries modes: i) Transmission geometry (Debye-Scherrer) ii) Reflection geometry (Bragg-Brentano). Comparing theses two modes irradiated volumes differences are observed: Any analytical technique requires a representative sample or sampling. Irradiated volume in diffraction is a key issue since higher volume yields enhanced particle statistics. According with the geometry used the irradiated volume is around 5 mm^3 in the case of transmission mode and 2 mm^3 with reflection geometry (Cuesta et al. 2014d) and cu radiation. Furthermore, Mo radiation can also be used to enhance the irradiated volume (Cuesta et al. 2014d).

1.5.2. Rheological measurements

When cement is mixed with water, each phase dissolves at least partially, leading to the establishment of supersaturated solution with respect to different hydrates, which can precipitate. As all chemical reactions, they obey the laws of thermodynamics and kinetics (Roussel 2012).

In rheology the graph representation of the correlation between shear stress and shear rate defining the flow behaviour of a liquid is called the “Flow Curve” (see figure 1.13. a). Another way to show the flow behaviour is through “Viscosity curve”, the correlation between viscosity and shear rate here is represented (see figure 1.13. b). Both types of curves are used in order to know the behaviour of cement pastes and the corresponding mortars and concretes; the workability/flowability, the effect of use of additives, the effect of different w/c ratios, and so on. Once cement is rheologically characterized, it is possible to improve the workability/flowability of mortars/pastes (Banfill 2006) and to obtain more homogeneous mixtures and hence, improved mechanical properties in general. Moreover, the setting evolution of cement pastes can be also followed at very early hydration times by following their viscosity values with time at a fixed shear rate, or even through oscillatory measurements.

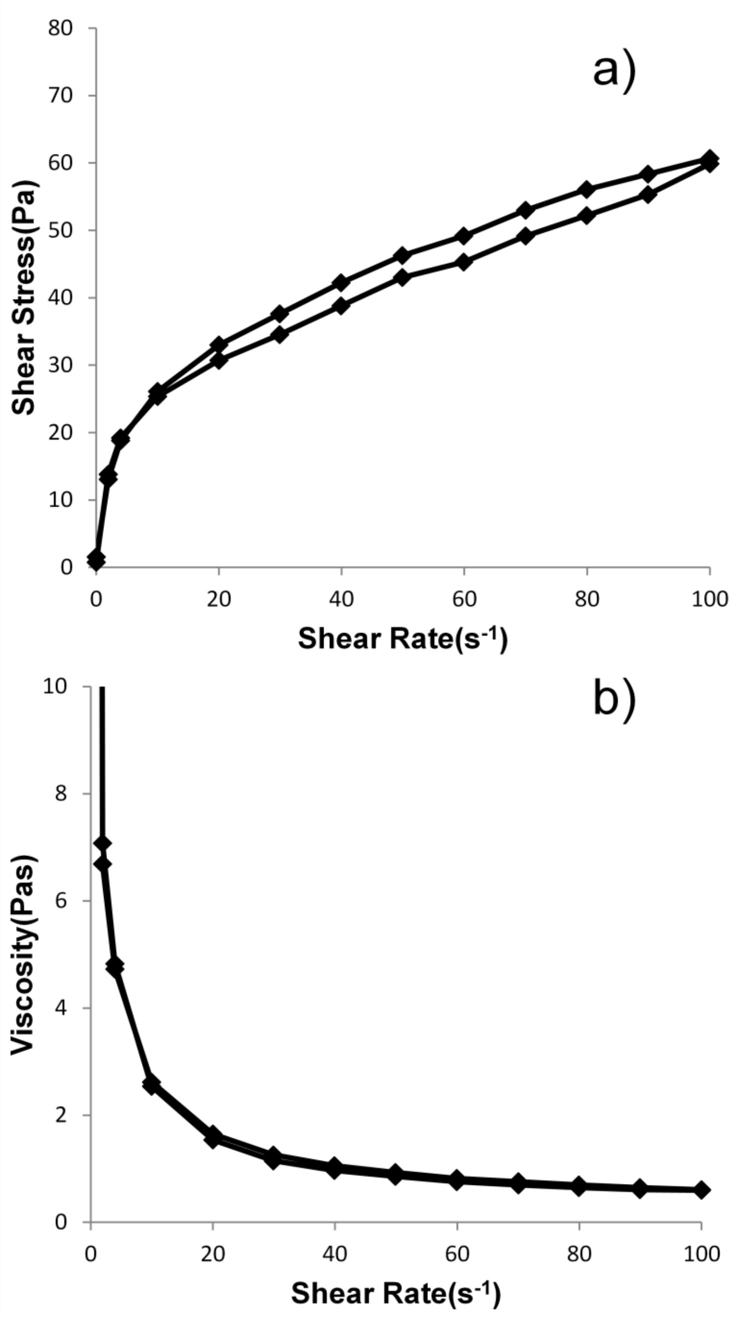

Figure 1.13. Examples of a) flow curve and b) viscosity curve of CSA cement paste (A25CSA; w/c=0.5).

1.5.3. Impedance Spectroscopy

The electrical properties of cement pastes attracted the interest of the scientists from the beginning of the last century (Schulte et al. 1978). The electrical conductivity (or inversely the electrical resistivity) of a cement paste can also be used as an indication for the setting and structural changes (Whittington et al. 1981; McCarter and Currant 1984; Morsy 1999; Levita et al. 2000; Salem 2002; Wei and Li 2006; Liao et al. 2011; Topcu et al. 2012). Conductivity usually increases rapidly immediately after mixing due to the dissolution of anhydrous cement phases. Then, the interaction between dissolved ions in the mixing solution leads to the precipitation of cement hydrates. The consumption of ions and the decrease in their mobility due to progressive structuring of the paste are responsible for a decrease in the conductivity, which is sharp when the massive precipitation of hydrates occurs.

Champenois (2013) suggested two stages which could define the thermal, electrical conductivity and also rheological behaviour (Figure 1.14.). This first stage corresponded to the induction period, during which only few anhydrous phases were dissolved, as shown by the small rise in temperature of the paste. Thus, the electrical conductivity values showed little variation during this period. The second stage occurred simultaneously with the acceleration of hydration, corresponding to the massive dissolution of anhydrous phases, and resulting in the rapid increase in the temperature of the paste. The second stage could thus be divided into two sub-periods (noted II-a and II-b in Figure 1.14.). In step II-a, the mineralogical analyses showed an accelerated consumption of ye'elimite, and the precipitation of significant amounts of ettringite. The electrical conductivity decreased sharply, which resulted from two factors: (a) the strong decrease in the mobility of the ionic species due to the progressive depercolation of the porous network caused by the precipitation of large amounts of hydrates and (b) a possible variation in the composition of the interstitial solution. During step II-b, the temperature reached its maximum before decreasing. Similarly, the electrical conductivity increased slightly before diminishing. This diminishing could be explained by the coalescence of the hydrate nuclei growing at the surface of the cement grains: the hydration rate decreased since the growing surface decreased. Once the anhydrous cement grains were entirely covered by hydrates, the hydration rate was then limited by diffusion through the product layer and became smaller and smaller as the thickness of this layer increased.

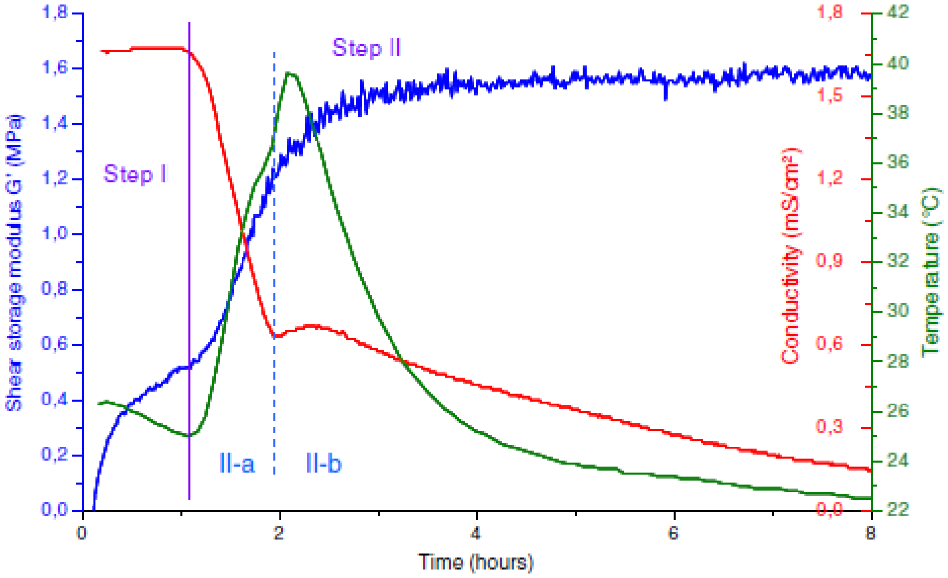

Figure 1.14. Evolution of the shear storage modulus, conductivity, and temperature during hydration of CSA cement (Champenois et al. 2013)

In order to collect simultaneously impedance spectroscopy measurements and temperature values during the first hydration time a K type thermocouple in the middle of the impedance measurement cell was including. According to that a home-made cell which measures simultaneously both (impedance spectroscopy and temperature) in cement pastes was performed. This consists on a hermetic cell with a prismatic shape (30x30x50 mm) made of expanded polystyrene (EPS) and two stainless steel electrodes located inside. Figure 1.15. shows a drawing of this cell.

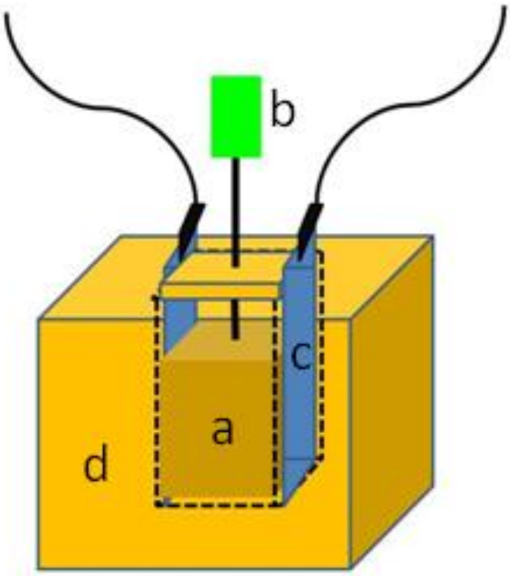

Figure 1.15. Home-made cell to Impedance Spectroscopy measurement: a-Sample; b-Thermocouple; c-Stainless steel electrodes; d-expanded polystyrene container.

2. Objectives

2. Objectives

CSA cements based on clinkers rich in calcium sulphoaluminate phase, also called ye’elimite ($C_4A_3\underline{S}$), and typically in combination with belite and calcium-aluminoferrites, are produced in significant quantities for niche applications. They also have the potential for more widespread applications as low-energy cements with an exceptionally low carbon footprint. Although ye'elimite-containing cements are very promising, their use is limited in Europe by the few standards concerning special cements derived from non-Portland clinkers. Hence, the general aim of this PhD Thesis is to better understand (and help in the control) the behaviour of these cements pastes during hydration. The specific objectives are described below:

i) To establish a reproducible methodology of processing and characterisation of hydrated CSA cement pastes, including the quantification of ACn (Amorphous and Crystalline not-quantified) content.

ii) To correlate phase assemblage of CSA cement pastes with the compressive strength measurements of the corresponding mortars (at laboratory scale).

iii) To understand the effect of the amount of gypsum, water to CSA cement ratio (w/CSA) and/or water to binder ratio (w/b), superplasticizer content and the possible substitution of CSA clinker by fly ash, as supplementary cementitious material (SCM), on the rheological behaviour, hydration process and mechanical properties of the corresponding mortars.

iv) To obtain tailored CSA cements and mortars with selected properties and thus, applications by using different types of sulphate sources and different kinds and amounts of retarders .

3. Articles section

Article#1 (a#1)

Advances in Cement Research

Amorphous determination in calcium sulfoaluminate materials by external and internal methods
García-Maté, Santacruz, Cuesta *et al.*

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Amorphous determination in calcium sulfoaluminate materials by external and internal methods

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External standard methodology has been successfully applied to quantify the known amounts of amorphous component that are increasingly added to cement-related materials. The consistency and accuracy of the methodology were demonstrated by the R^2 values of the least-square fits determined against weighed amorphous amounts, which were close to 1·0 in all the series. This method requires common laboratory X-ray powder diffractometers (knowing the equipment constant) and avoids the dilution/alteration of the sample. However, the obtained values may be biased due to poor particle statistics. On the other hand, internal standard analysis in transmission geometry is suitable to determine the absolute amorphous and crystalline non-quantified contents that are less biased owing to enhanced particle averaging statistics. This method is, however, experimentally tedious due to the addition of the internal standard and the sample loading in the X-ray diffraction sample holders which represent inherent drawbacks to follow amorphous evolutions.

Introduction

Cements based on clinkers rich in the calcium sulfoaluminate phase, also called ye'elimite (C_4A_3s), typically in combination with belite and calcium-aluminoferrites, are produced in significant quantities for specialty applications, and also have the potential for even more widespread application in the future as low-energy cements with an exceptionally low carbon footprint (Aranda and De la Torre, 2013; Gartner, 2004; Pérez-Bravo *et al.*, 2013). Quantitative analysis of such clinkers, and also of their hydration products, is an essential part of the research process needed to better understand how they hydrate and thus how their performance can be modified for any given application. The only method readily available for quantitative phase analysis of these materials in the laboratory is quantitative X-ray diffractometry (XRD) coupled with Rietveld analysis. However, the absolute accuracy of such methods is very dependent on the 'degree of crystallinity' of the solids present, as 'X-ray amorphous' phases cannot be directly measured. Thus, some way of accurately estimating the total mass of material that is not detected directly (and which hence is considered to be 'X-ray amorphous') is needed. The research described in this paper was aimed at improving the accuracy of these methods, especially as applied to cement rich in calcium sulfoaluminate (De la Torre *et al.*, 2001; Jansen *et al.*, 2011a; O'Connor and Raven, 1988; Walenta *et al.*, 2002).

Materials and methods

Materials

Two different sulfobelite clinkers produced by Lafarge (France), codes K171p3 and LHY-04097-53, and two supplementary cementitious materials (SCM), a fly ash (FA) and a natural limestone (LS), were studied. Glass powder, obtained by grinding very thin optical glass plate by hand in an agate mortar for 30 min, was also used in this work. Table 1 gives the elemental analysis for the raw materials determined by X-ray fluorescence (XRF) measured in a Magic X spectrometer (Panalytical, Almelo, The Netherlands) using the calibration curve of silica-alumina

Article#2 (a#2)

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Rheological and hydration characterization of calcium sulfoaluminate cement pastes

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ABSTRACT

Calcium sulfoaluminate (CSA) cements are currently receiving a lot of attention because their manufacture produces less CO_2 than ordinary Portland cement (OPC). However, it is essential to understand all parameters which may affect the hydration processes. This work deals with the study of the effect of several parameters, such as superplasticizer (SP), gypsum contents (10, 20 and 30 wt.%) and w/c ratio (0.4 and 0.5), on the properties of CSA pastes during early hydration. This characterization has been performed through rheological studies, Rietveld quantitative phase analysis of measured X-ray diffraction patterns, thermal analysis and mercury porosimetry for pastes, and by compressive strength measurements for mortars. The effect of the used SP on the rheological properties has been established. Its addition makes little difference to the amount of ettringite formed but strongly decreases the large pore fraction in the pastes. Furthermore, the SP role on compressive strength is variable, as it increases the values for mortars containing 30 wt.% gypsum but decreases the strengths for mortars containing 10 wt.% gypsum.

1. Introduction

Calcium sulfoaluminate (CSA) cements are receiving increasing attention nowadays since their manufacture produces less CO_2 than ordinary Portland cement (OPC) [1–4]. These binders may have quite variable compositions, but all of them contain Ye'elimite phase, also called Klein's salt or tetracalcium trialuminate sulfate ($C_4A_3\underline{S}$) [5]. Cement nomenclature will be used hereafter $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\underline{S} = SO_3$, $M = MgO$, $T = TiO_2$ and $H = H_2O$. The term CSA cements is usually reserved for those clinkers containing more than 50 wt.% of Klein's salt and they may also have minor amount of phases such as C_2S, CA, C_4AF, CS, $C\underline{S}H_2$, and so on [6]. Cements with large amounts of Ye'elimite may have special applications such as high strength developments at early-ages [7,8] and radioactive element encapsulation in a high-density cement paste [9,10]. On the other hand, a new related type of cement is emerging, aimed to replace OPC in the long term by combining approximately 20–30 wt.% of Ye'elimite (for early-age strength development) and 50–60 wt.% of activated belite (for medium-age strength development) [11–13]. This type of cement, initially developed in China but without the key activation of belite, is known as sulfobelite and also as belite-calcium sulfoaluminate cement to stress the importance of belite in its composition and performance.

CSA cements are prepared by mixing the clinker with different amounts of a calcium sulfate set regulator such as gypsum, bassanite or natural anhydrite, or mixtures of them. Their main properties are high early strengths, short setting times, impermeability, sulfate and chloride corrosion resistance and low alkalinity [5]. The early hydration of the CSA cements is mainly governed by the amount and reactivity of the added calcium sulfate [8,14–16]; it gives as main crystalline phases ettringite and monosulfate [17] and most of the hydration heat is released during the first 12–24 h of hydration [18]. The w/c ratio needed for full hydration is higher than that for an OPC. For instance, pure Ye'elimite reacting with the stoichiometric amount of anhydrite to yield ettringite requires a 0.78 w/c ratio [17,19] which may yield pastes with larger pore diameters than OPC pastes. Moreover, both high and low w/c ratios may involve severe expansion [20] with high w/c ratios also resulting in final strength development problems [21]; however, lower particle size [20] or the use of additives may eliminate some of these undesirable properties [22].

The dispersion of agglomerated cement particles is a key point to improve the workability of concrete to obtain more homogeneous mixtures and to reduce the amount of mixing water [23,24]. This is the role of superplasticizers and their use has become a common practice in OPC. It has been demonstrated that a lower water demand, within certain limits, is related with improved mechanical properties [25,26]. This is because the adsorption of the superplasticizers onto the surface of cement particles causes the repulsion of the particles (electrostatic or electrosteric). This repulsion depends [23] on the type and amount of

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Article#3 (a#3)

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Hydration studies of calcium sulfoaluminate cements blended with fly ash

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ABSTRACT

The main objective of this work is to study the hydration and properties of calcium sulfoaluminate cement pastes blended with fly ash (FA) and the corresponding mortars at different hydration ages. Laboratory X-ray powder diffraction, rheological studies, thermal analysis, porosimetry and compressive strength measurements were performed. The analysis of the diffraction data by Rietveld method allowed quantifying crystalline phases and overall amorphous contents. The studied parameters were: i) FA content, 0, 15 and 30 wt.%; and ii) water addition, water-to-CSA mass ratio (w/CSA = 0.50 and 0.65), and water-to-binder mass ratio (w/b = 0.50). Finally, compressive strengths after 6 months of 0 and 15 wt.% FA [w/CSA = 0.50] mortars were similar: 73 ± 2 and 72 ± 3 MPa, respectively. This is justified by the filler effect of the FA as no strong evidences of reactivity of FA with CSA were observed. These results support the partial substitution of CSA cements with FA with the economic and environmental benefits.

1. Introduction

Calcium sulfoaluminate (CSA) cements are receiving increasing attention since their manufacture produces much less CO_2 than ordinary Portland cement (OPC) [1–5]. In addition, they show interesting properties such as high early-age strengths [6–8], short setting times, impermeability [9,10], sulfate and chloride corrosion resistance and low alkalinity. The main uses of these CSA cements, or blended with Portland cements, are for quick repairs and pre-cast products or floor concrete applications [11]. All these properties are related to the resulting hydration phases at the first hours of hydration. Early hydration of CSA cements [12,13] gives ettringite also named as AFt ($C_6AS_3H_{32}$), and monosulfate also known as AFm (C_4ASH_{12}) [14], as main crystalline phases, depending mainly upon the sulfate availability. CSA binders may show variable compositions, but all of them contain ye'elimite, also called Klein's salt or tetracalcium trialuminate sulfate (C_4A_3S) [1,15]. Ye'elimite synthesis produces only a third part of the CO_2 released by the production of alite content in OPCs [16]. Moreover, its clinkering temperature (~1250 °C) is lower than that for OPC clinkers, consequently there are environmental benefits due to fuel savings. Ye'elimite-containing clinkers are easier to be ground than OPC clinkers, and waste materials or industrial by-products can be used in the kiln feed as raw material.

Another environmental strategy for reducing the negative impact of the cement industry is the partial substitution of cement by by-products materials (such as fly ash or slag) also known as supplementary cementitious materials (SCMs) [17–19]. The environmental benefits of the use of waste materials are two folds, lower CO_2 emissions because of the clinker reduction, and the valorization of a "useless" product. Furthermore, the addition of SCMs to cement may give the possibility of the modification of their properties [20] and mortars/concretes prepared from blends, such as decreased hydration heat, improved workability of fresh mortar/concrete mix, improved chemical resistance, ultimate strength increase, and improvement of other engineering properties of concrete [21]. However, the extent of replacement is limited by the following problems: reduced early strength, limited amounts of reactive SCMs and limited replacement by non-reactive SCMs without compromising final strength. In any case, it is essential to control/understand the hydration process [14,22,23] without or with SCMs. The effect of the addition of by-products to OPC pastes has already been well described in literature [24,25]. However, for CSA cements, it is needed to understand all parameters involved in the CSA-SCMs hydration, and the key roles of water and SCMs contents. The w/c ratio required for full CSA hydration is higher than that for an OPC [26]. The specific water demand for complete hydration will depend on CSA phase assemblage (mainly ye'elimite and belite contents). For instance, pure ye'elimite reacting with the stoichiometric amount of anhydrite to yield ettringite requires a 0.78 w/c mass ratio [14,27]. This means that a CSA with ~50 wt.% of ye'elimite would need a w/CSA ratio of 0.5, which may yield pastes with larger pore diameters than OPC pastes. Moreover, high w/c ratios may involve severe expansion [28] also resulting in poor final strengths; however, lower initial particle sizes or the use of additives may reduce some of these undesirable properties [26,29,30].

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Effect of calcium sulfate source on the hydration of calcium sulfoaluminate eco-cement

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ABSTRACT

The availability of cements, including eco-cements, with tailored mechanical properties is very important for special applications in the building industry. Here we report a full study of the hydration of calcium sulfoaluminate eco-cements with different sulfate sources (gypsum, bassanite and anhydrite) and two water/cement ratios (0.50 and 0.65). These parameters have been chosen because they are known to strongly modify the mechanical properties of the resulting mortars and concretes. The applied multi-technique characterization includes: phase assemblage by Rietveld method, evolved heat, conductivity, rheology, compressive strength and expansion/retraction measurements. The dissolution rate of the sulfate sources is key to control the hydration reactions. Bassanite dissolves very fast and hence the initial setting time of the pastes and mortars is too short (20 min) to produce homogeneous samples. Anhydrite dissolves slowly so, at 1 hydration-day, the amount of ettringite formed (20 wt%) is lower than that in gypsum pastes (26 wt%) (*w*/*c* = 0.50), producing mortars with lower compressive strengths. After 3 hydration-days, anhydrite pastes showed slightly larger ettringite contents and hence, mortars with slightly higher compressive strengths. Ettringite content is the chief parameter to explain the strength development in these eco-cements.

1. Introduction

The manufacture of Calcium SulfoAluminate (CSA) cements is more environmentally friendly than that of OPC [1–4] as their production releases up to 40% less CO_2 than the latter (this reduction depends on CSA composition). The main performances of CSA cements are fast setting time (followed by a rapid hardening), good-chemical resistance properties and, depending on the amount of the added sulfate source they are self-levelling materials or shrinkage controllers [5,6]. In addition, they show high early strengths, good impermeability, sulfate and chloride corrosion resistance and low alkalinity [7].

CSA cements present a wide range of phase assemblages, but all of them contain over 50 wt% calcium sulfoaluminate (also known as yéelimite, Klein's salt, $Ca_4Al_6SO_{16}$ or $C_4A_3\overline{S}$), jointly with belite, ferrite and other minor components [8–14]. Cement nomenclature will be used hereafter: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $T = TiO_2$, $\overline{S} = SO_3$, $\overline{C} = CO_2$ and $H = H_2O$.

CSA cements are prepared by mixing the clinker with different amounts of a calcium sulfate set regulator such as gypsum ($C\overline{S}H_2$), bassanite ($C\overline{S}H_{0.5}$) or anhydrite ($C\overline{S}$), or mixtures of them. Furthermore, it is possible to modify the hydration process of CSA cements not only by its composition, but also by the selection of different quantities [15] or sources of calcium sulfate [5,16–19].

During the hydration process [18,19], three main issues take place: (i) dissolution of crystalline anhydrous phases, (ii) appearance of new phases such as crystalline ettringite (a.k.a. AFt), and amorphous gels such as aluminate hydroxide hydrate (AH_3); and (iii) consumption of free water. The precipitation can be summarized as follow: yéelimite in presence of a sulfate source (gypsum, bassanite or anhydrite) and in aqueous medium will form ettringite and gibbsite (AH_3), according to Eqs. (1)–(3), respectively. AH_3 precipitates as a poorly-crystallized or amorphous phase [2]. Most of the hydration heat is released during the first 24 h of hydration [20]. Furthermore, bassanite will also react with water to form gypsum and will release heat, according to Eq. (4).

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4. General results and discussion

4. General result and discussion

X-Ray diffraction is a well known technique to determine and quantify the phases present in crystalline materials. I am a member of a working group which has a vast experience in anhydrous cements and clinkers characterization by X-Ray powder diffraction combined with Rietveld methodology. During my research time I would like to highlight my contribution in the processing and characterisation of hydrated CSA cement pastes, including the quantification of ACn (Amorphous and Crystalline not-quantified) content, and the measurement of mechanical properties (compressive strength) of the corresponding mortars.

This PhD Thesis is focused in the influence of different issues, such as, the water to cement and water to binder ratios, type and amount of sulphate sources, fly ash additions and the use of superplasticizer and retarders on CSA cement pastes and the corresponding mortars.

4.1. Cement paste storage, characterisation and processing

To establish a methodology to work with cement pastes was a challenge at the beginning of this PhD. Firstly the processing and storage of hydrated cements were optimised. Standards were followed for paste preparation, but the curing/storing methodology evolved. Initially, methacrylate sample holders (at 20±1 ºC and 99% relative humidity) covered with a glass casing were used to store the pastes until measurements were performed; this procedure gave irreproducible results and segregations. The final methodology was that the cement pastes are poured into hermetically closed polytetrafluoroethylene (PTFE) cylinder shape moulds and rotated at 15 rpm during the first 24 hours at 20±1 ºC; these samples are demoulded after 24h and stored within deionised water at 20±1 ºC until the age of study. With this procedure, we have achieved homogenous cement pastes avoiding the undesired drying effect during hydration.

In order to use the minimum amount of sample (laboratory studies) in mortars compressive strength measurements, moulds with dimensions of 30x30x30 mm were used. Firstly these moulds were made of silicone, but those ones made of steel yielded to much more reproducible results.

Additionally, a methodology to stop hydration was established to further characterize the CSA cement pastes (article a#3).

4.1.1. ACn quantification: Comparison of external and internal standard methodologies

The quantitative phase analysis of cements, and also of their hydration products, is an essential part of the research process needed to better understand how they hydrate and thus how their performance can be modified for any given application (Pelletier-Chaignat et al. 2012). X-ray diffraction coupled with Rietveld analysis is a suitable method to obtain quantitative phase analysis of these materials in the laboratory. However, the absolute accuracy of this method is very dependent on the "degree of crystallinity" of the phases which are present. Anhydrous cement samples are mainly crystalline materials; however it is necessary to quantify the amorphous/sub-cooled phases and also misfitting problems of the analyzed crystalline phases and any crystalline phase non-included in the Rietveld control file. In previous studies, we used internal standard in reflection geometry to calculate the ACn content with good results. However, the addition of an internal standard may alter the cement hydration reactions, dilute the phases in the pastes, and produce microabsorption problems and so on. Hence, studies with external standard in reflection geometry combined with the G-factor approach have been also analyzed and compared with measurements using internal standard. The research described in article a#1 was aimed to check the accuracy of these two methods (external standard in reflection geometry and internal standard in transmission geometry), especially as applied to cements rich in calcium sulphoaluminate to determined the ACn content. This work was carried out in collaboration with Lafarge Research Center (LCR).

Figure 4.1. shows the calculated ACn values using the G-factor method for four studied samples. The measured samples were two clinkers (K171p3 and LHY-04097-53) and one limestone, where different amounts of glass (G) where added. Each family (solid symbols) is plotted as a function of the added glass (xG). Open symbols stand for the ACn value obtained by the same methodology for the samples without added glass. All R^2 (coefficient of determination which indicates the goodness of fit) values were close to 1.0, showing the consistency of the methodology. This proves that the increasing of ACn content in a crystalline mixture can be successfully quantified by this external-standard methodology. In addition, the direct measurement values (obtained from samples without any glass addition) and the value calculated from the intercept of the best fit line were compared. In LHY-04097-53 clinker these values matches very well, Figure 4.1.c, however in the rest of the cases the direct values were slightly overestimated. In figures 4.1.a and b (Clinker K171p3 mixed with glass by two different operators using different mixing methodologies) this slight overestimation in the ACn content may be explained by the presence of large particle sizes (sharper diffraction peaks), which may have a negative effect in the particle statistics in powder diffraction (De la Torre and Aranda 2003; Westphal et al. 2002). Moreover, in the sample of figure 4.1.d (limestone) this overestimation phenomenon may be due to the preferred orientation (PO) which is also related to particle statistic distribution, shown by this sample, which was corrected by using March-Dollase algorithm (Dollase 1986). The ACn content of limestone was measured in triplicate, and it

can be observed that the pattern with the lowest P.O. ratio, meaning the highest degree of orientation, yielded the largest overestimation of the ACn value (Table 3 in article a#1), confirming the negative effect of poor particle statistics distribution in the G-factor methodology.

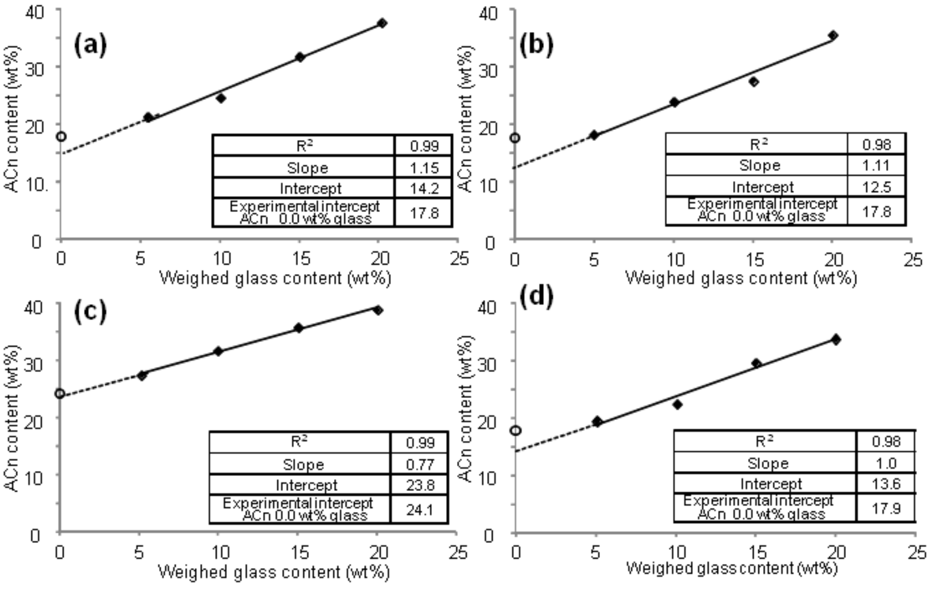


Figure 4.1. ACn content using external standard (reflection geometry), in weight percentage, as a function of the amount of added glass for (a) K-xG, (b) K-xG-LCR, (c) LHY-xG and (d) LS-xG. Inset included least-squared fit data.

The internal standard methodology in transmission geometry was also used to derive ACn contents in those samples for which the intercept and the experimental ACn values obtained through the external standard methodology did not match. This was performed to check if relatively poor particle statistics was playing a role in the systematic overestimation of ACn by the external standard methodology. Working in transmission with a focused X-ray beam enhances particle statistics distribution because a larger sample volume is tested. Transmission geometry gives two beneficial effects: i) lower preferred orientation; and ii) larger analyzed sample volume. This combination resulted in a smaller average ACn value, 9 wt% (Table 3 in article a#1), confirming that an enhanced particle statistics distribution diminished the ACn value.

On the one hand, we can conclude that the increase of the amorphous and non-quantified crystalline solid contents (ACn) in a mixed powder can be followed using both, internal and external standard, where the latter is of even greater utility in the study of hydration of cement pastes. This method has the inherent benefit of using common experimental requirements of LXRPD (knowing the diffractometer constant) and moreover, the sample is not altered/diluted by introducing any internal standard.

On the other hand, the internal standard methodology in transmission geometry is useful to corroborate and scale the values obtained by the external standard methodology (reflection geometry). Internal standard analysis in transmission allowed us to derive ACn contents that were less biased because the particle averaging statistics were enhanced. However, this approach is not very suitable for following ACn evolution in a process because it is experimentally tedious due to the addition of the internal standard and the sample loading in the LXRPD sample holders.

4.1.2. Porosimetry

An important factor influencing the durability of cement systems is their permeability. However, as the permeability is difficult to measure, it is common to focus instead on pore microstructure measurements. The pore structure greatly influences the permeability as well as other properties such as compressive strength and ionic diffusion. Mercury intrusion porosimetry (MIP), among other techniques, have been utilised in pore structure analysis. This method requires samples to be dried to empty the pores of any existing water with concomitant danger of irreversible alteration of the porosity. Furthermore, cement pastes are particularly sensitive to the drying method used. A number of various methods are used in the literature, although focused mainly on hydrated OPC pastes (Zhang and Scherer 2011). Zhang and Glasser (2000) showed that ettringite (AFt) and monosulphate (AFm) phases in cement pastes are particularly sensitive to the drying method used. Due to this, ettringite-rich cement pastes tend to be more sensitive than OPC pastes to the drying method used.

According to that, an experimental work (writing article) was carried out using ettringite-rich hardened (at least 120 days old) cement paste samples comparing the different drying methods found in the literature. Concluding that mineralogical damage occurs to CSA samples exposed to prolong drying times and harsh drying methods. D-drying and isopropanol exchange methods for drying and arresting hydration of CSA based samples, showed the lower levels of pastes deterioration.

4.2. Raw materials characterisation

A commercial Calcium sulphoaluminate clinker (CSA), industrially produced in China and marketed in Europe by BELITH S.P.R.L. (Belgium), a commercial micron natural gypsum also marketed by BELITH S.P.R.L. (Belgium) and a class F fly ash (FA), ASTM C618, from the power station of Lada (Spain) were used as raw materials. Although in article a#2 the clinker was labelled CS10, in articles a#3, a#4 and in this text will be named CSA. The elemental composition of these raw materials determined by X-ray fluorescence (XRF) is given in Table 4.1.

The mineralogical compositions of the three raw materials (CSA, gypsum and fly ash) were determined by RQPA methodology combined with G-factor approach (see table 4. 2.). Figure 4.2.a shows the Rietveld plot of CSA clinker and figure 4.2.b the fly ash Rietveld plot, both with main peaks labelled. The ACn content of

Table 4.1. XRF analysis for the raw materials (CSA clinker, gypsum and fly ash).

Oxides	**CSA (wt%)**	**Gypsum (wt%)**	**Fly Ash* (wt%)**
Al_2O_3	33.80	0.37	26.40
CaO	41.97	31.20	4.53
Fe_2O_3	2.37	0.12	7.45
K_2O	0.25	0.054	3.56
SiO_2	8.20	0.73	52.70
MgO	2.73	0.098	1.93
P_2O_5	0.13	0.44	0.28
TiO_2	1.50	-	0.96
SO_3	8.80	42.40	-
SrO	0.15	2.38	-
Cr_2O_3	0.017	-	-
MnO	0.011	-	0.05
ZrO_2	0.070	-	-
Na2O	<0.08	0.20	0.53
LoI	-	22.00	1.60

*Fernádez-Jímenez et al. 2008.

this CSA clinker, ~23 wt%, is slightly higher than that found for OPC clinkers, ~10 wt% (Suherman et al. 2002; Whitfield and Mitchell 2003), likely due to the lower clinkering temperature leading to smaller particle sizes and microstrains and defect-bearing crystals. The crystal structure descriptions for each clinker phase were those detailed elsewhere (article c#1), except for ye'elimite, where a reviewed orthorhombic $C_4A_3\underline{S}$ has been used (Cuesta et al. 2013). The gypsum has some impurities (anhydrite and sodium and strontium sulphates) and about 17 wt% of ACn (see table 4.2.). And finally, the ACn content in FA is ~85 wt%, where mullite and quartz and some other crystalline minor phases (hematites, magnesium-ferrite, lime and periclase) are present as crystalline fraction (see figure 4.2.b and table 4.2).

Table 4.2. RQPA for the three raw materials (CSA clinker, gypsum and fly ash).

Phases	**CSA (wt%)**	**Phases (wt%)**	**Gypsum (wt%)**	**Phases**	**Fly Ash**
$C_4A_3\underline{S}$-ortho	50.9	$C\underline{S}H_2$	78.8	Mullite	8.4
β-C_2S	16.1	$C\underline{S}$ III	2.1	Quartz	5.3
CT	4.7	$SrSO_4$	1.9	Hematites	0.4
M	2.4	Na_2SO_4	0.4	Magnesium-Ferrite	0.5
C_4AF	1.5			Lime	0.2
C_2MS_2	0.9			M	0.2
$C\underline{S}$ II	0.5				
ACn	23.1		16.8		85

In addition, thermal results (DTA-TGA) of gypsum (see Figure 4.3.) show a weight loss of 19.0 wt%. As the theoretical weight loss of gypsum is ~ 20.9wt% (molecules of water), it means that the used gypsum contains some impurities; it was corroborated with XRF and RQPA results; the gypsum purity is around 95%. Figure 4.3. shows two endothermic peaks, point 1 corresponds to the evaporation of the first 1.5 molecules of water and point 2 with last 0.5 molecules of water.

Moreover the fineness values determined for CSA and gypsum were 480 and 500 m^2/kg, respectively.

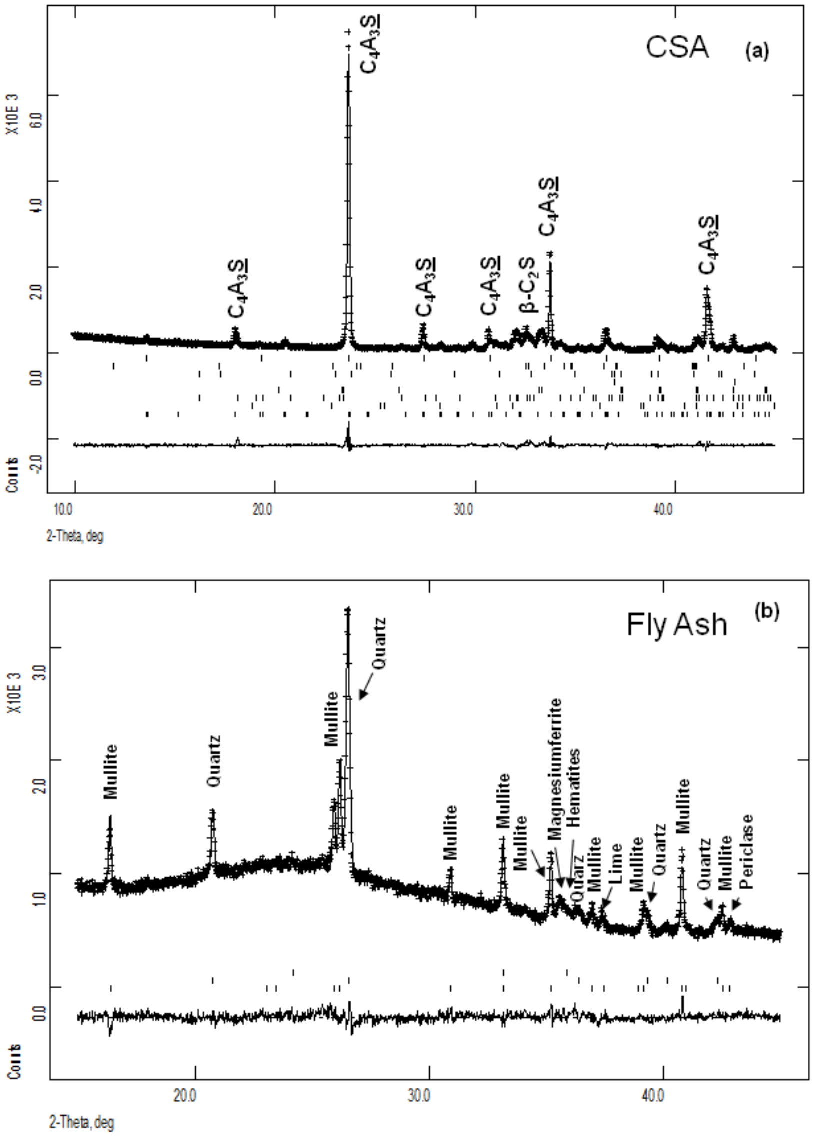


Figure 4.2. Selected range of the Rietveld plot for (a) anhydrous CSA cement and (b) fly ash. Crosses are the experimental scan, solid line is the calculated pattern and the bottom line is the difference curve. The major peaks for each phase are labeled.

In addition, three additives were used: i) a commercial policarboxilate-based superplasticizer, Floadis 1623 (Adex Polymer S.L., Madrid, Spain), with 25 wt% of active matter, labelled PC for its composition (in articles a#2 and a#3 was labelled SP); ii) tartaric acid (Adex Polymer S.L., Madrid, Spain) was dissolved in water (10 wt%), named TA and iii) nitrilotris(methylene)phosphonic acid (Sigma-Aldrich) was also dissolved in water (5 wt%), labelled PA. TA and PA are used as retarders.

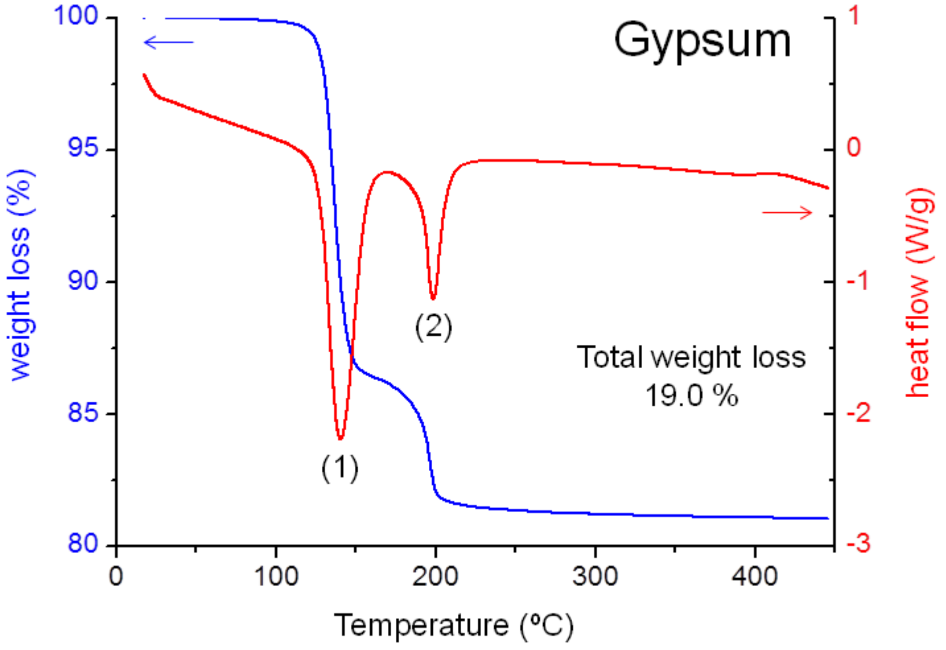


Figure 4.3. DTA-TGA curves for gypsum.

4.3. Cement paste optimisation

Understanding the behaviour of ye 'elimite rich eco-cement is essential. To do so, the effect of the amount of gypsum, water to cement ratio (w/c), superplasticizer content and the possible addition of fly ash were studied. This was performed through studies of the rheological behaviour, hydration processes and porosity of pastes and mechanical properties of the corresponding mortars (a#2 and a#3 articles).

i) Gypsum content

Cements were prepared by mixing the clinker with different amounts of a calcium sulphate set regulator (gypsum). The amount of the added sulphate source (Pelletier-Chaignat et al. 2012; Glasser and Zhang 2001; Pera and Ambroise 2004) plays a key role in controlling the hydration of ye'elimite and the final performances of pastes/mortars/concretes. Hence, three different amounts of gypsum (10, 20 and 30 wt%), named GxCSA, where x is 10, 20 or 30 stands for the added amount to the clinker. The mineralogical changes of the cement pastes with ongoing hydration were quantified through LXRPD. From the data of the hydrated pastes shown in the tables 4 and 5 in article a#2, it can be observed that $C_4A_3\underline{S}$ and $C\underline{S}H_2$ contents decreased after 3, 7 and 28 (only measured with 30 wt% of gypsum) days; the most important reduction was observed within the first 3 hydration days (Zhang and Glasser 2002). And in general, most of the hydration heat evolution occurred at 7 days, and between 7 and 28 days hydration proceeded very slowly with very little changes (see figure 4.4.).

In the case of G30CSA and G20CSA pastes, $C_4A_3\underline{S}$ and gypsum content decreased but they were not completely depleted. For G10CSA pastes, the $C_4A_3\underline{S}$ content was not depleted but gypsum content was exhausted. When gypsum was depleted, the hydration progressed by precipitation of calcium monosulphoaluminate hydrate (see section 1.2.5.). This was confirmed by DTA-TGA. Figure 4.5. shows the DTA-TGA curves for G30CSA (Fig. 4.5.a) and G10CSA (Fig. 4.5.b) pastes (w/c=0.50 with PC) at 7 days of hydration. Both figures show an endothermic peak at 100 ºC (point 1) mainly due to the weight loss of water of ettringite (Winnefeld and Lothenbach 2010). In the case of the pastes with the higher amount of gypsum (30 wt %) (Fig 4.5.a) a small endothermic peak at 125 ºC (point 2), that likely corresponds to the weight loss from gypsum (Winnefeld and Lothenbach 2010) appeared. However, this gypsum peak was not observed in cement pastes with 10 wt % of gypsum (Fig. 4.5.b), because this phase was exhausted during hydration. Concomitantly, a small peak appeared at 150 ºC (point 3), corresponding to an AFm phase.

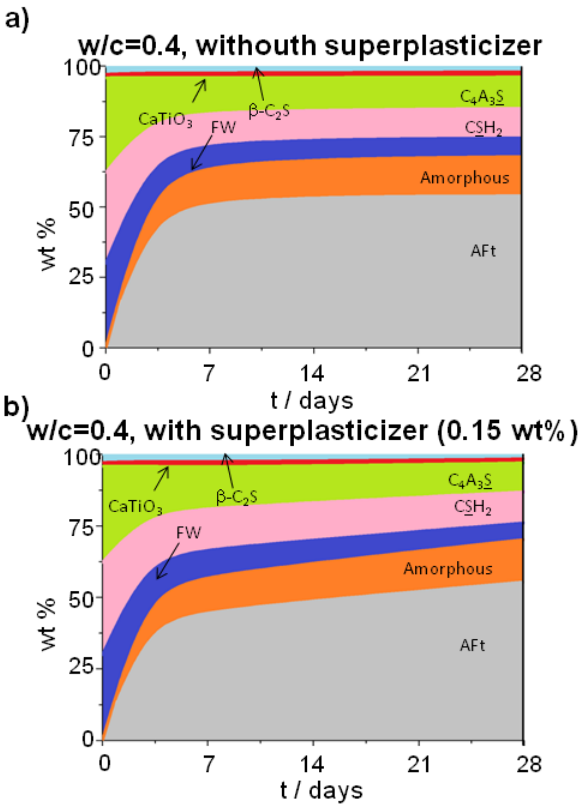


Figure 4.4. Phase assemblage evolution for G30CSA; (a) w/c=0.40 without; and (b) with superplasticizer.

ii) Water to CSA ratio content (w/CSA)

The effect of water to CSA cement ratio was studied in article a#2, where cement pastes with 10, 20 and 30 wt% of gypsum were prepared at w/CSA ratios of 0.40

and 0.50. Moreover, the w/CSA ratios for mortars were slightly higher than for pastes in order to achieve a good homogenization (0.50 and 0.60). In addition, in article a#3 the water additions studied were w/CSA=0.50 and 0.65 and water-to-binder ratio (w/b) of 0.50 in cement pastes and mortars with FA (0, 15 or 30 wt%).

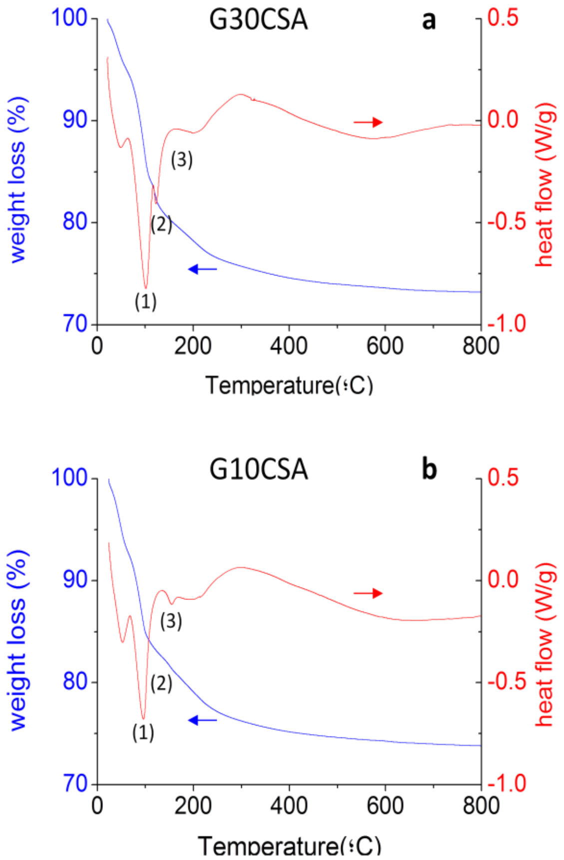


Figure 4.5. DTA-TG curves for G30CSA (a) and G10CSA (b) pastes after 7 days hydration.

In general, large amounts of unhydrated/undissolved $C_4A_3\underline{S}$ and gypsum and low precipitation of ettringite were evolved with low w/c ratios (see table 4 and 5 in article a#2), hence the lower w/c ratio, the lower degree of hydration. Moreover, pore distribution was affected by the w/CSA ratio. By increasing the w/CSA content, the average porous diameter increased and the compressive strength values of mortars with lower w/CSA ratio always gave higher values than those derived from mortars with higher w/CSA (see table 4.3.), as expected.

Table 4.3. Compressive strength for CSA mortar (at 7 days of hydration) at different water to cement ratio. The water addition is expressed in both w/CSA and w/b for all pastes. The numbers in parentheses are the standard deviations of three measurements.

Cement mortars	**Strength – 7 days (MPa)**			
	w/CSA=0.50	w/CSA=0.60	w/CSA=0.65	w/b=0.50
G30CSA*	41(1)	37.6(6)	-	-
G20CSA*	48(1)	40.9(9)	-	-
G10CSA*	50.0(6)	35(1)	-	-
G30CSA; PC*	45.6(5)	39.2(8)	-	-
G20CSA; PC*	46.1(9)	37.0(5)	-	-
G10CSA; PC*	39.3(9)	35.1(4)	-	-
G25CSA-0FA$^{\#}$	64.5(6)	-	48.8(7)	64.5(6)
G25CSA-15FA$^{\#}$	65.2(9) w/b=0.42	-	49.1(8) w/b=0.55	56.2(8) w/CSA=0.59
G25CSA-30FA$^{\#}$	56(4) w/b=0.35	-	45(1) w/b=0.46	44.2(7) w/CSA=0.71

*Performed in silicone moulds; $^{\#}$ Performed in steel moulds

Since the knowledge of the water/solid ratio is a key point to understand the hydration of cements, this was also studied in article a#3 where the fly ash role was also investigate. In this case w/c=0.50 and 0.65 were studied and we discard 0.40, because it was insufficient (a#2). In addition the water-to-binder mass ratio (w/b) of 0.50 was also studied. Samples were cast in hermetically closed cylinders and after 24h left in water at 20 ºC. It is worth highlighting that after 180 hydration days a small amount of free water is still remained in the pastes, determined by DTA-TGA showing no drying effects in any samples. In agreement with article a#2, by increasing the water to cement ratio, higher degree of reaction was determined. In this way, w/CSA=0.50 mortars always yielded higher mechanical strengths than the analogous w/CSA=0.65 mortars, or w/b=0.50 (see Table 4.3.). This was correlated with porosity values.

iii) Superplasticizer content

As it was observed, lower water to cement ratios yields higher compressive strength values (Table 4.3.) within a certain limit. Hence, when the right type and amount of additive, such as superplasticizers (water-reducing substances) are added to CSA pastes with low w/c ratios; these pastes show a better dispersion of particles, consequently, improved mechanical performance are attained. The amount of policarboxilate-based superplasticizer (PC) added to the GxCSA (where x is 10, 20 or 30 wt% of gypsum) pastes, with w/c=0.40 was optimised through the study of their rheological behaviour (a#2). Figure 4.6. shows flow curves of G30CSA of pastes at w/c=0.40 and different superplasticizer contents. In general, pastes (w/c=0.40) without SP showed a shear thinning behavior and high viscosity values; the addition of a small amount of PC (0.10 wt%) drastically reduced the viscosity of the pastes (from around 2.6 to around 0.25 Pa·s at 50 s^{-1}) and minimum viscosity values were obtained after the addition of 0.15, 0.15 and 0.20 wt% PC for G30CSA, G20CSA and G10CSA, respectively (inset in Figure 4.6. where G30CSA is highlighted). The gypsum content did not present an important effect on the viscosity of the pastes in the studied range. These optimum values were also used for w/CSA=0.50 pastes.

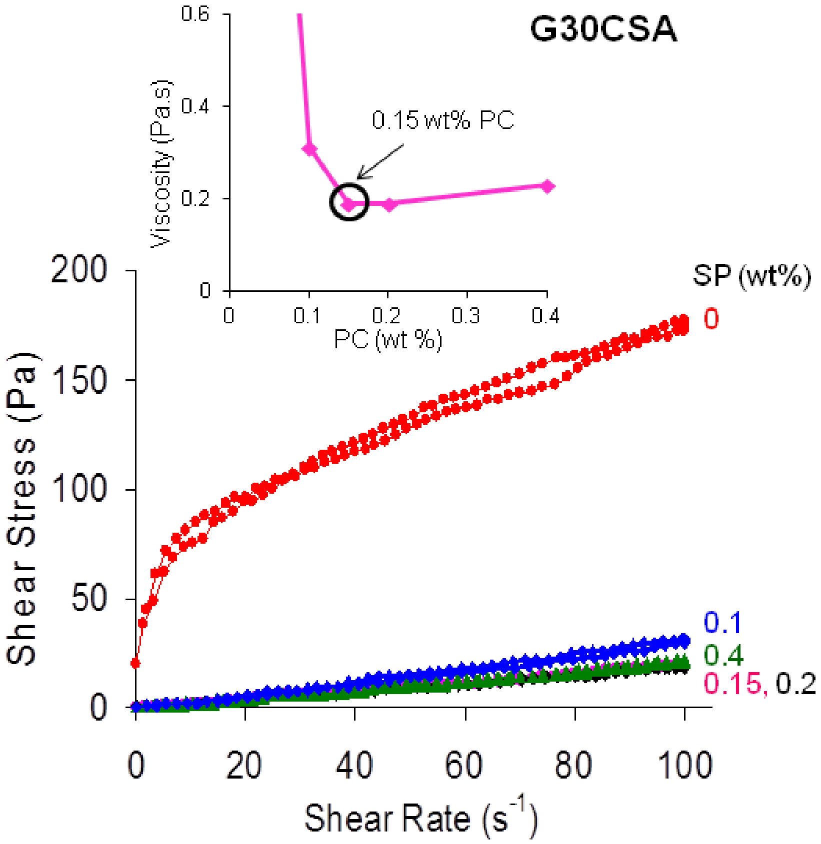


Figure 4.6. Flow curves for G30CSA pastes at w/c=0.40 and different superplasticizer contents. The insets show the deflocculation curve of G30CSA pastes at 50 s^{-1} (shear rate). The optimum amount of PC is highlighted.

Once the PC amount was optimised the phase assemblage of the cement pastes with time was studied to assure that they were not modified by this addition. It was performed through LXRPD measurements and RQPA. Figure 4.4. depicts an example of the phase assemblage with evolution of the hydration time of cement pastes with 30 wt% of gypsum (G30CSA). There were no relevant differences in the phase assemblages within the first 28 days between pastes with or without superplasticizer. It may be stated that reaction kinetics were slightly slowed down by PC. Moreover, the addition of PC to a paste with the same w/c changed the bimodal pore distribution to a monomodal one, eliminating the larger pores. Consequently, mortars with higher mechanical properties were obtained.

Before we finished this section, we must note that 30 wt% of gypsum yielded an important decrease in the compressive strength values. Article a#2 showed that the optimum gypsum content to have the highest compressive strengths should be between 10 and 20 wt %. This result was in full agreement with the RQPA of the pastes, since gypsum was completely depleted in G10CSA pastes but there was a significant remaining amount in G20CSA pastes. And it must be noted that G10CSA and G20CSA mortars with w/c ratio of 0.5 gave compressive strength values similar to those of OPC mortars. However, AFt (ettringite) is the most desired hydrated phases because provides high strengths; and although, the best compressive strength values were obtained for mortars with 10 and 20 wt % of gypsum, the stoichiometric amount of gypsum necessary to prepare our cements is close to 30 wt %, taking in consideration the content of ye'elimite in our CSA clinker to obtain AFt. Due to these reasons, the gypsum content selected for the following studies was 25 wt % (G25CSA).

iv) Fly ash (FA) additions

The addition of FA has mainly two environmental benefits, firstly lower CO_2 emissions due to the clinker reduction and secondly the valorization of an “useless” product. Furthermore, it supposes an economic saving. Moreover, compressive strength of the corresponding mortars could be higher if the pozzolanic effect occurs. The pozzolanic reaction is the chemical reaction that occurs in OPC pastes between calcium hydroxide, also known as Portlandite (CH) and reactive acid species, present (or developed) in SCMs, forming C-S-H or related gels, which provides mortars with even higher compressive strengths. In CSA cements instead of portlandite, gibbsite (AH_3) is formed (mainly by equation [1.3] in the introduction); and the possible reaction between gibbsite and acid species to give a related gel was studied. So, the effects of the amount of fly ash (0, 15 and 30 wt%) and possible pozzolanic effect were analysed by LXRPD, rheological studies, thermal analysis and porosimetry in cement pastes and compressive strength measurements of the corresponding mortars up to 180 days of hydration (article a#3).

First of all, viscosity and water demand of the pastes were studied, through the rheological measurements. FA shows a lower water demand than CSA cement at very early hydration times. Because of that, at the same water to binder (w/b) ratio, the viscosity values decreased by increasing the fly ash content and for the same viscosity value the corresponding w/b ratio decreased by increasing the FA content (Figure 2 b in a#3). This behavior would give the possibility of preparing blended pastes with FA at lower w/b ratios, with the same viscosity than those without any FA addition, which may reduce the porosity of the cements and hence increase the compressive strength values of the corresponding mortars. Hence, these studies would allow the preparation of tailored pastes with specific viscosity by selecting both w/CSA or w/b ratio and FA content. Finally, cement pastes with the same w/CSA ratio showed higher viscosity values by increasing the fly ash content, due to the increasing of the total solid contents.

Pozzolanic reaction in CSA systems may involved AH_3 phase. These cements contained belite (β-C_2S). The degree of hydration of belite was enhanced by increasing water addition, as expected. This phase react with water and AH_3 to give stratlingite (Li et al. 2007a; Winnefeld and Lothenbach 2010; Álvarez-Pinazo et al. 2013). In our studied pastes, this phase was only present in some pastes hydrated for 180 days. However the measured stratlingite measured at 180 days decreased from 1.1 wt% (0 wt% of FA) to 0.4 wt% and 0.0 wt% by adding 15 and 30 wt% FA, respectively. This result may indicate that FA was reacting with AH_3, and thus this aluminum source was not longer available to react with C_2S to form stratlingite. Nevertheless, these differences were too small to ensure the pozzolanic reaction. Moreover, the amount of measured stratlingite contents were always much lower than those expected values taking into account the diminution of belite up to 180 days, in agreement to Winnefeld and Lothenbach (2010) and Álvarez-Pinazo (2013). Therefore, we have to infer, that in these systems, belite was reacting mainly to give an amorphous phase, likely a C-S-H type gel.

Cement pastes with the same w/CSA ratio and with 15 wt % of FA produced mortars with similar or slightly higher compressive strength values than the corresponding ones without FA (72.9 and 71.6 MPa at 180 days of hydration to G25-w/c=0.50 with 0 and 15 wt% of FA, respectively) due to the filler effects. However, higher amounts of FA produced a dilution effect, which was not compensated by the filler effect, causing mortars with lower mechanical strength values (66.9 MPa with 30 wt% of FA). Hence, the addition of fly ash affects in two different ways, firstly acts as filler and secondly dilutes the cement. Finally, this was confirmed through porosity studies, when fly ash was added to the pastes, the corresponding porosity values decreased. Moreover, the dilution effect of the FA addition, for a fixed w/b ratio, was exacerbated due to the higher w/CSA ratios, and hence the filler effect was neglected, which caused mortars with lower mechanical strengths (72.9, 64.4 and 48.4 MPa at 180 days of hydration to G25-w/b=0.50 with 0, 15 and 30 wt% of FA, respectively). These findings were also strongly correlated with the porosity of the corresponding pastes.

4.4. ACn content characterization

As it was discussed in the introduction, ACn composition is not possible to be determined directly, hence, in article a#3 the possible ACn composition (sulphate, aluminate and calcium groups behaviour as a function of time) was suggested thought RQPA and Rietveld methodology combined with G-factor in CSA-FA (0, 15 or 30 wt% of FA) for w/CSA=0.50 and 0.65 and w/b=0.50.

i) Sulphate groups

The amount of reacted/dissolved sulphate was determined from the disappearance of ye'elimite and gypsum and the amount of crystallized sulphate was determined from the appearance of ettringite and silicon-free AFm (Figure 4.7.). The dotted lines indicate the maximum sulfate that can crystallize based on mass balance. We observed that only a percentage of the dissolved sulphate was crystallized, an average of 40% of the total sulphate content may be in pore solution or within ACn phase(s). The dissolved, but not crystallized, sulphate content values were much higher than those that can be in the pore solution (Winnefeld and Lothenbach 2010), thus it must be inferred that a significant part of the sulphate content was included in the ACn fraction, as ill-crystallized AFm phases.

ii) Aluminate groups

Figure 4.8.a shows the evolution with time of aluminate groups. The unreacted aluminates (x-FA-res) have been calculated taking into account the remaining $C_4A_3\underline{S}$ and crystallized aluminates (x-FA-cryst) from crystalline AFt, AFm and stratlingite. The dotted lines indicate the maximum aluminate that can crystallize. Only a small percentage of the dissolved aluminates were crystallized (25-30%), and thus 70-75% of the total aluminates content may be mainly as ACn phase(s). Due to the alkaline character of the pastes, Al^{3+} ions might well be forming $Al(OH)_3$, which was mainly poorly-crystallized or an amorphous phase.

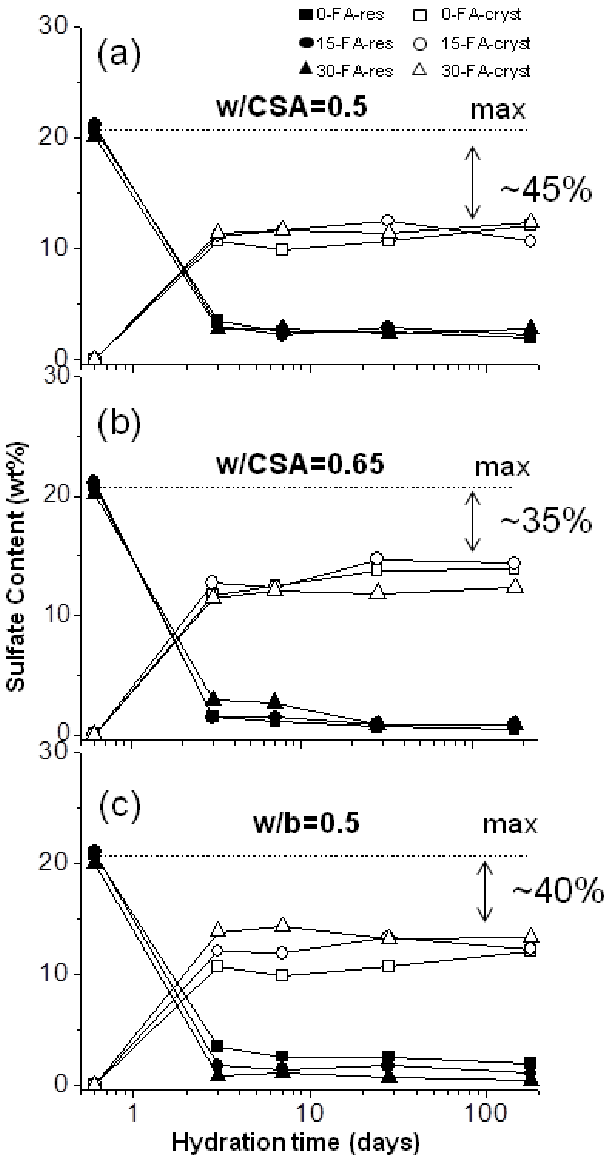


Figure 4.7. Weight percentage of sulfate groups as a function of time, (a) w/CSA=0.50, (b) w/CSA=0.65 and (c) w/b=0.50. Solid symbols (x-FA-res) stands for the remaining gypsum and $C_4A_3\underline{S}$ contents and open symbols (x-FA-cryst) stands for crystallized ettringite, both expressed as sulfate groups percentage.

iii) Calcium groups

Unreacted calcium content was determined from the remaining gypsum, $C_4A_3\underline{S}$ and β-C_2S amounts and crystallized calcium stood for the calcium cation included in the crystalline AFt, AFm and stratlingite phases (see figure 4.8.b). Around 35% of the total calcium content may be jointly with sulphate in the pore solution and as part of ACn phase(s), such as ill-crystallized AFm. In Figure 4.8.b the dotted lines, as in previous figures, indicate the maximum Ca^{2+} that can crystallize referred to the previously dissolved calcium ions. Moreover, the formation of an amorphous gel, similar to C–A–S–H was not dismissed, although further research is required.

Finally, the main conclusions of this hydration study were: i) FA showed higher water demands than CSA; ii) $C_4A_3\underline{S}$ and gypsum were almost completely dissolved within the first three days of hydration where the main precipitating crystalline phase was AFt; iii) ACn may be poorly crystallized phases, such as AFm or gel-type phases with stoichiometries close to AH_3 and C-A-S-H; iv) Belite reactivity was enhanced by high w/c and; v) Porosity decreased with: hydration time, low water cement ratios, FA additions (filler effects with 15 wt% of FA), affecting mechanical strengths with the expected trend (the higher porosity the lower mechanical values); vi) The partial substitution of CSA cement by 15 wt% of had a positive effects enhancing (or at least not reducing) mechanical strengths, mainly due to filler effect; vii) Higher FA additions, had a negative effect in mechanical strengths due to dilution effect; viii) With a fixed w/b ratio, the compressive strength decreased by increasing the amount of FA, due to the higher water content (higher porosity values). With these conclusions we can said that partial substitution of cement by FA involves economic and environmental benefits. Moreover, the chemical reactions during hydration in presence of FA do not change which may suggest that durability is not compromised.

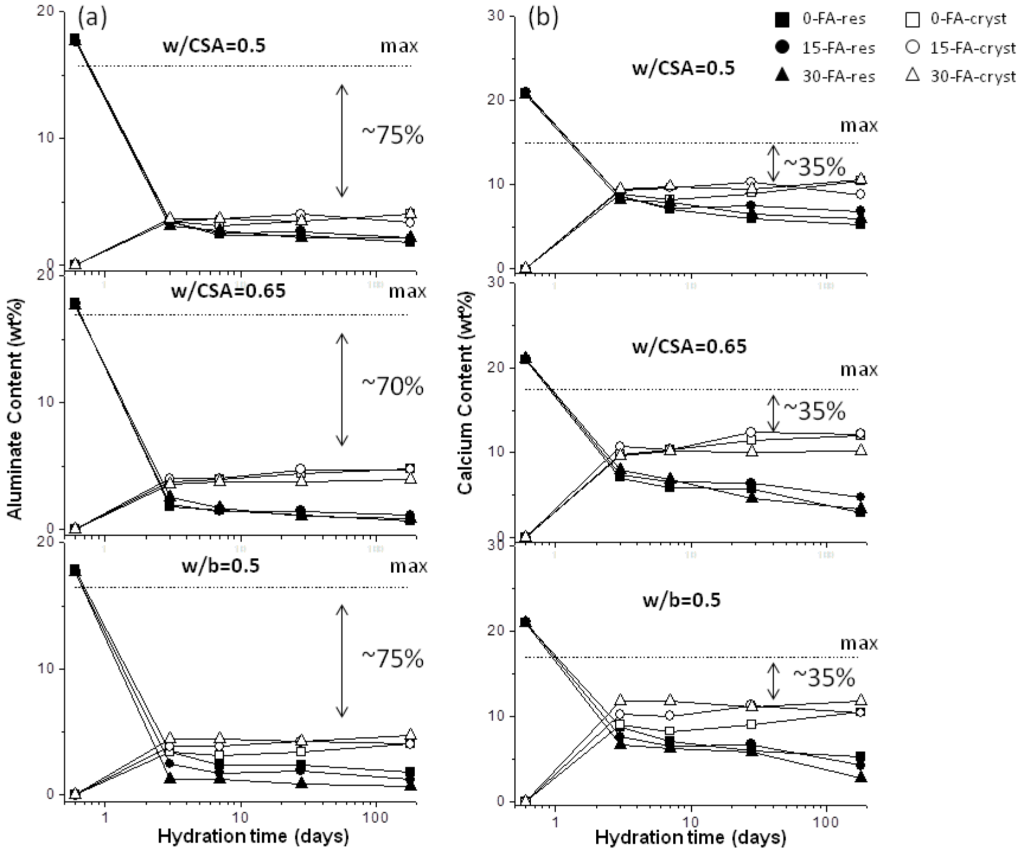


Figure 4.8. (a) Weight percentage of aluminate groups as a function of time. x-FA-res stands for the remaining $C_4A_3\underline{S}$ contents and x-FA-cryst stands for crystallized AFt, AFm and stratlingite, both expressed as aluminate groups percentage; (b) Weight percentage of Ca^{2+} groups as a function of time. x-FA-res stands for the remaining gypsum, $C_4A_3\underline{S}$ and β-C_2S contents and x-FA-cryst stands for crystallized AFt, AFm and stratlingite, both expressed as Ca^{2+} percentage.

4.5. Tailored cements

In the following studies, ACn content was always studied thought RQPA and Rietveld methodology combined with G-factor, due to the trusted result obtained in article a#3 and supported by article a#1 which concluded that this methodology is of great utility in the study of hydration of cement pastes

Once a good knowledge of the CSA clinker was achieved and the effect of several issues, such as water addition, gypsum content and FA substitutions were under control, the following step was to obtain tailored CSA cements and mortars for different applications; using different kinds of sulphate sources and retarders additions. And with that we can modify the rheological behaviour, setting times, and so on. Always keeping in mind that corresponding mortars always should have high compressive strengths.

Special applications in the building industry require cements, including eco-cements, with tailored properties.

Because of that, in this Thesis a full study of the hydration of CSA cement prepared with 25 wt% of different sulphate sources (gypsum, bassanite or anhydrite) and the same water/cement ratios (0.50 and 0.65) have been performed (article a#4). Moreover, the use of additives (retarders) in bassanite-pastes and mortars was studied (writing article). Both bassanite and anhydrite were prepared from commercial gypsum through the corresponding heating treatments. Phase assemblage, evolved heat, conductivity and rheology of cement pastes and compressive strength and expansion/retraction of mortars were studied.

i) Sulphate source

Setting time of cement pastes with gypsum, bassanite and anhydrite (see table 4.4.) are in agreement with solubility trend of each sulphate source (0.88, 0.24 and 0.21 g/100 mL for bassanite, gypsum and anhydrite at 20 ºC, respectively). Bassanite pastes (B) showed the fastest initial setting time, 20 min, independently of the water content. Gypsum pastes (G) showed intermediate initial setting time values, which was independent of the water content and anhydrite pastes (A) showed the slowest initial setting time, being even longer for w/c=0.65.

Table 4.4. Initial setting time of all the studied pastes.

Paste	Initial setting time
G-w/c=0.50	190 min
G-w/c=0.65	190 min
B-w/c=0.50	20 min
B-w/c=0.65	20 min
B+0.020PC-w/c=0.50	20 min
A-w/c=0.50	320 min
A-w/c=0.65	~11 h

Due to the short setting times of bassanite cement pastes, heterogeneous mortars with poor mechanical properties were produced. And also, bassanite pastes with water to cement ratio 0.50 had the highest viscosity. Since our aim was to compare the effect of the source of sulphate during the hydration of the cement, and how it affected to the mechanical properties of the corresponding mortars, the fresh pastes should have similar viscosity values. To reduce the viscosity of the bassanite paste (w/c=0.50), different amounts of PC (policarboxilate-based superplasticizers) were added. The addition of 0.015 wt% of PC diminished the viscosity (from 4.7 to 1.6 Pa·s at 50 s^{-1}) and the rheopectic cycle (from -13650 to -3500 Pa·s^{-1}); but, this was not enough to show similar rheological behavior than G and A pastes, which showed viscosity values of 1.0 and 0.8 Pa·s at 50 s^{-1}, respectively, and small rheopectic cycles (-800 and -280 Pa·s^{-1}, respectively), figure 4.9.a. However, when 0.020 wt% of PC was added to the bassanite-paste, the rheological behavior of this paste at very early ages was similar to those prepared with gypsum or anhydrite (w/c=0.50), showing even lower viscosity, 0.6 Pa·s at 50 s^{-1}, and an intermediate rheopectic cycle, -440 Pa·s^{-1} (see figure 4.9.a). In addition, setting times were not affected by these PC additions. Pastes with w/c ratio of 0.65 were also measured and showed lower viscosity values than those with 0.50, as expected. Furthermore, these fresh pastes prepared with gypsum and anhydrite (w/c=0.65) showed a very similar rheological behaviour. B-pastes with w/c=0.65 with and without PC were not further characterized due to the poor mechanical properties of the corresponding pastes/mortars.

The evolution of the viscosity of all these pastes was studied with time (Figure 4.9.b). This evolution of viscosity with time for all the studied pastes was measured at a shear rate of 4 s^{-1}. This selected shear rate is low enough for not destroying the structure and high enough for obtaining trustable data. B-paste with 0.020 wt% PC (w/c=0.50) showed relatively low initial viscosity values but its viscosity showed a sharp increase and achieves 600 Pa·s in less than 10 minutes of hydration. This is related with the quick bassanite dissolution and hence quick ettringite formation. When PC is not added into the bassanite paste, the increasing in viscosity was even faster. The viscosity of gypsum and anhydrite pastes increased at slower pace than that of bassanite pastes, where the A-paste was the slowest one for w/c=0.65, within the first 130 min of hydration. Although G and A pastes with w/c=0.65 showed similar initial viscosity values, the gypsum paste showed a marked increase of viscosity after 75 minutes (Figure 4.9.b). This is a complex process where different parameters are evolved. The hydration of cement pastes is a process of ions dissolution, ions saturation, and a final precipitation of new phases, such as ettringite. From the rheological point of view, the dissolution of cement phases would reduce the solids loading which may decrease the viscosity; however, the increase in ions content would decrease the electric double layer around the particles and hence will enlarge the viscosity; in addition, the presence of new solid phases also would increment the viscosity, although the ions concentration (ionic conductivity) would be lower. Moreover, ettringite particles usually show a prismatic/needle shape that it is known to yield a more dramatic effect on the viscosity than spherical particles (Moreno 2005).

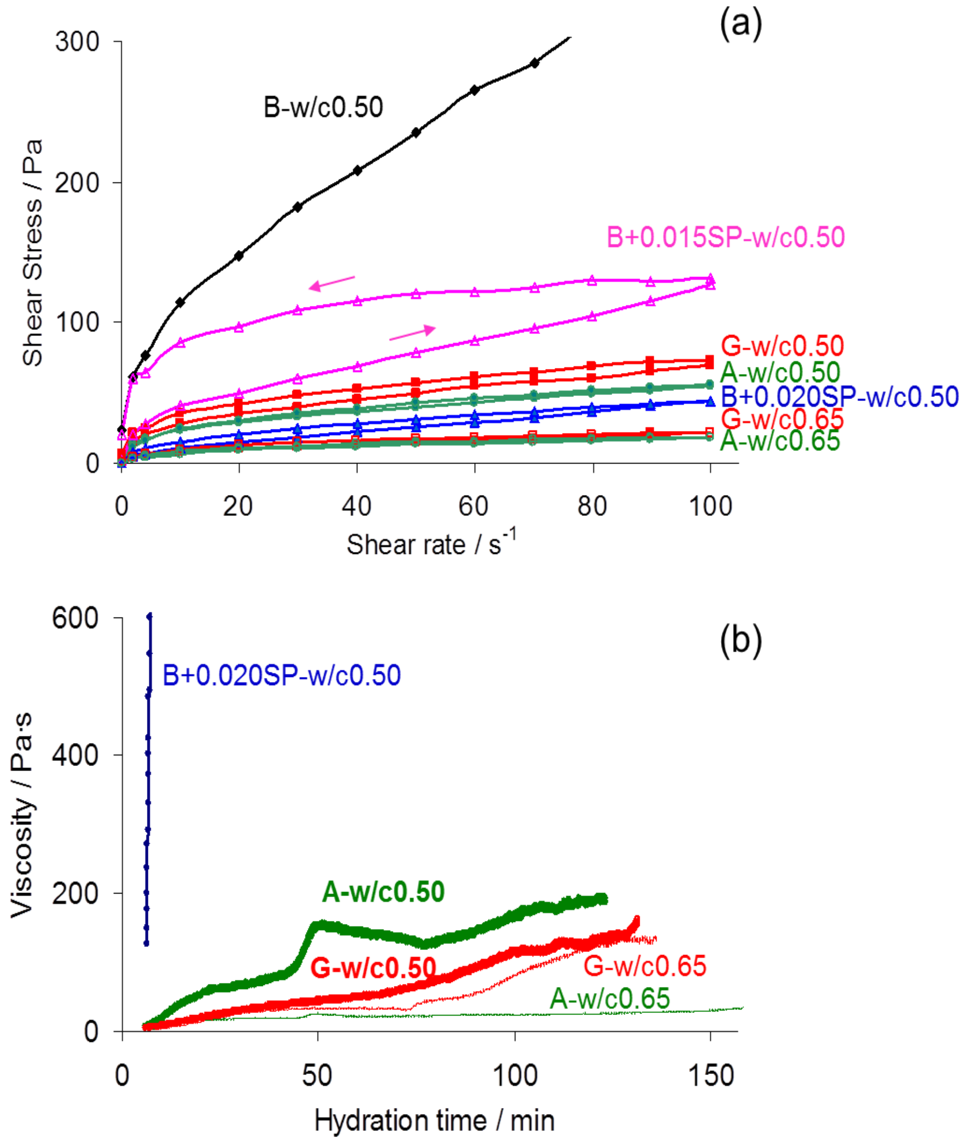


Figure 4.9. (a) Flow curves and (b) viscosity vs. time curves at a shear rate of $4s^{-1}$ of the cement pastes with the different sulphate sources.

To follow the hydration process, these pastes were further characterised through (w/c=0.50 with similar viscosity values) impedance spectroscopy and temperature studies during the first hours. For that, a home-made cell which measures simultaneously both impedance spectroscopy and temperature of cement pastes was designed (Figure 1.15. in introduction). As expected, the conductivity of all pastes decreased after a few minutes of hydration. All pastes showed a specific value of conductivity at the beginning of the hydration between 0.020-0.030 S·cm^{-1}. At that time, the temperature started to increase up to a maximum value which is coincident with a point close to the minimum value of conductivity (see figure 4.10.). Bassanite pastes with 0.020 wt% PC and without PC showed similar behaviour. Differences on conductivity and temperature between G, B and A pastes started just after 20 min of hydration. Both bassanite pastes released high amounts of heat (these pastes achieved temperatures ~80°C) in a very short time (~100 min), and the conductivity was negligible just after 200 min of hydration. This very large amount of released heat may be explained by the initial dissolution of bassanite and precipitation of gypsum. This *new* gypsum progressively re-dissolved and ettringite was formed (see figure 4.11.b). G-paste showed an initial conductivity similar to that for B-pastes (~0.03 S·cm^{-1}); however, conductivity and temperature were kept constant within the first hour of hydration for G-pastes. Furthermore, a maximum temperature of only 45 °C was observed after 130 min, where the conductivity was still 0.015 S·cm^{-1}, which is ~0.0025 S·cm^{-1} after 10 hours. Finally, anhydrite pastes showed the lowest initial conductivity, ~0.020 S·cm^{-1}, and it started to decrease after 120 min. In addition, the maximum temperature, 52°C, happened after 270 min; this was due to the low solubility of anhydrite. After that time, the system continued with the hydration and its conductivity was almost negligible after 350 min. Summarizing, the temperature increased firstly for bassanite pastes, secondly for gypsum pastes, and finally for anhydrite pastes, following the trend of solubility; and also in agreement with the setting time of the corresponding pastes (Table 4.5.). A-w/c=0.50 paste showed lower initial ionic conductivity than G-w/c=0.50; this may be also related with its lower initial sulphate dissolution. All these effects might explain the higher viscosity values with time of A-w/c=0.50 pastes when compare with G-w/c=0.50 pastes (Figure 4.9.b). In addition, its concentration of ions decreased at a slower pace, being higher than the corresponding value for G-paste between 100 and 260 min of hydration.

Figure 4.10. depicts that in the three selected pastes (G25CSA, B25CSA+0.020 PC and A25CSA), maximum of temperature and minimum of conductivity agree. This was directly correlated with precipitation of hydrated phases (Champenois et al. 2013) and it was corroborated by an in-situ LXRPD study performed in transmission geometry with the addition of SiO_2 as internal standard to quantify ACn and free water content. Prior to that, we had to check if the addition of SiO_2 affected hydration behaviour. Similar AFt content were obtained for G-samples with and without SiO_2 after 1 day of hydration (28.1 and 29.4, respectively), indicating that the kinetic was not altered by the presence of SiO_2.

RQPA including ACn and free water contents for all pastes were measured in transmission mode from 0 min to 3 hours of hydration (Table 1 in article a#4). From these data, the transformation of bassanite into gypsum, and the dissolution of gypsum and anhydrite with time, and the formation of new phases, mainly AFt was followed. Comparing RQPA, conductivity and temperature results, we can confirm that the maximum of temperature and minimum of conductivity match with the precipitation of the main phase of hydration products (mainly AFt).

Figure 4.11. shows raw patterns of A-paste and B-paste with 0.020 wt% PC, both with w/c=0.50 at different hydration times, including the anhydrous in each case. From this figure, the evolution of different phases is clear; anhydrite and ye'elimite were slightly decreasing and minimum amount of ettringite appeared after 2h of hydration (Figure 4.11.a) In Figure 4.11.b bassanite was still present after 20 min of hydration but it have disappeared at 1 hour. Part of the bassanite has been transformed on gypsum after 20 min, and the latter was present even after 3 hours of hydration in a large amount. Moreover, ye'elimite was slightly decreasing with

time and ettringite content up to 1 h of hydration. This is also in concordance with the slower rate of dissolution of anhydrite when compared to gypsum or bassanite.

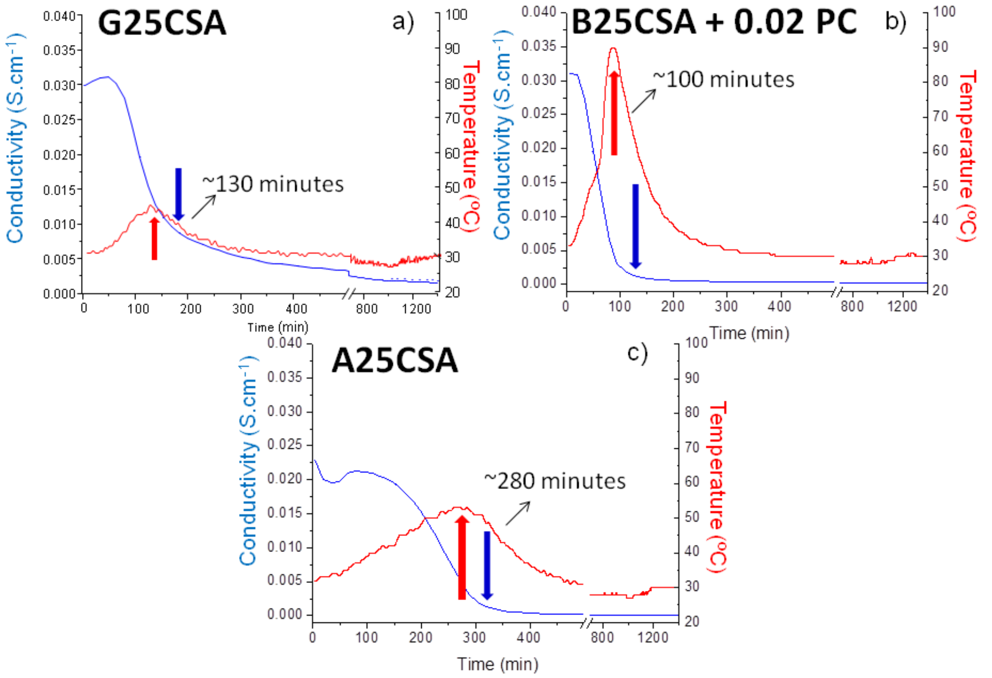


Figure 4.10. Impedance Spectroscopy and temperature results of (a) G-paste; (b) B-paste + 0.020 PC; and (c) A-paste.

The mechanical behaviour of the corresponding mortars was studied. From the analysis of the data it was clear that w/c=0.50 mortars always yielded higher compressive strengths than the analogous w/c=0.65 mortars. Furthermore, the role of the sulphate source was also very important. Figure 4.12. shows the compressive strength values of mortars (w/c=0.50) prepared from all pastes at 1 and 3 days of hydration times. On the one hand, reactions in B-pastes occurred very quickly, and their short setting time was enormously sensitive to the degree of homogeneity of the mortars, producing mortars with poor mechanical properties, as mentioned before. The addition of a small amount of PC improved the workability of the mortar but it does not delayed appreciably the setting time, hence, compressive strength increased, but was not comparable with gypsum and anhydrite values. On the other hand, G-mortars showed higher mechanical strengths at 1 day than those of A-mortars (Marchi and Costa 2011) at w/c=0.50 (40.7 and 21.2 MPa, respectively). However after 3 days, A-w/c0.50 mortars showed slightly higher compressive strengths than G-w/c0.50 mortars (64.1 and 59.0 MPa, respectively). This can be justified by the slow dissolution kinetic of anhydrite in comparison with gypsum; hence, after 1 day of hydration the formation of ettringite occurred at greater extent for G-pastes (inset Figure 4.12.), so G-mortars present higher mechanical strength at 1 day (the higher the ettringite amounts, the higher the mechanical strengths). All the same, similar ettringite contents were observed for both pastes (G-paste and A-paste) within the 3 hydration days (see inset in Figure 4.12); due to G-w/c0.50 and A-w/c0.50 mortars showed similar compressive strengths, being slightly higher for A, likely due to the plasticity (Winnefeld and Barlag 2009). The setting time for A-pastes was much longer than that for G-pastes yielding to pastes with a higher plasticity to better accommodate the precipitation of ettringite. In addition, it must be noted that G-w/c0.50 and A-w/c0.50 mortars gave compressive strength values higher than OPC mortars at very early age (3 days).

Finally, the longitudinal modifications of the mortars with hydration time were measured. The expansion (or shrinkage) experienced by mortars is mainly related to the nature of pore structure, which affects the mobility of ions and the available space to accommodate new phases. Both adequate deformability and strength values are required to allow expansion without the formation of cracks. Our study has revealed that B-mortars did not present enough plasticity to accommodate AFt precipitation with time, consequently higher expansions were observed. Gypsum and anhydrite had a small effect on the dimensional variation of CSA mortars, since the expansion/shrinkage was almost negligible (Figure 9 in article a#4).

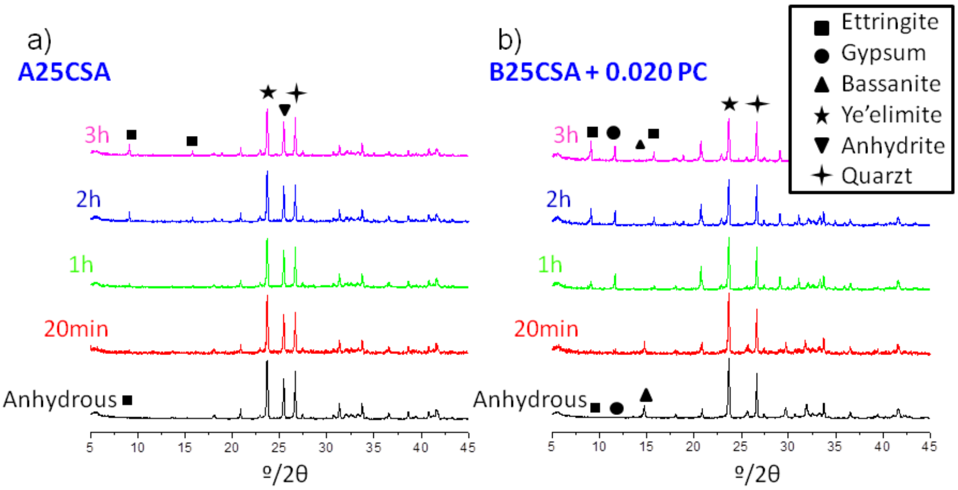
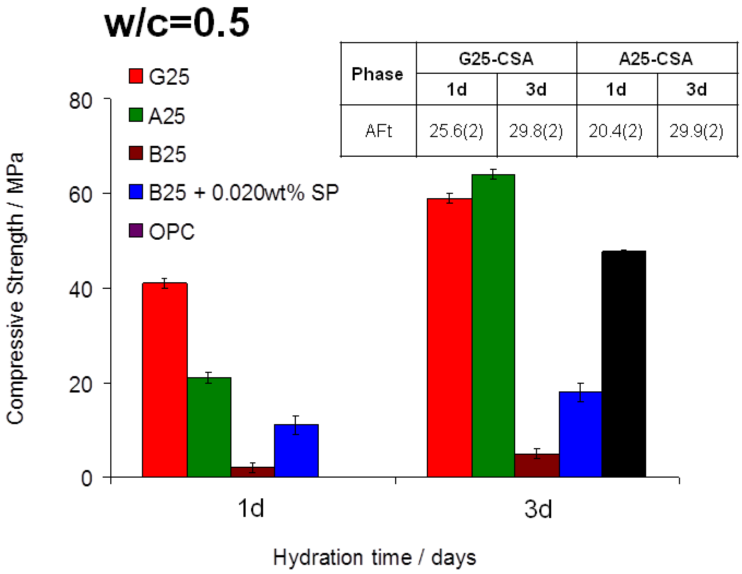


Figure 4.11. LXRPD diffractograms of (a) A-w/c0.50 and (b) B-w/c0.50 with 0.020 wt% SP at different hydration times (from 20 min to 3 hours) measured in transmission mode. The diffractogram of the anhydrous paste is shown for the sake of comparison.



Phase	G25-CSA		A25-CSA	
	1d	3d	1d	3d
AFt	25.6(2)	29.8(2)	20.4(2)	29.9(2)

Figure 4.12. Compressive strength values of mortars (w/c=0.5) prepared from all pastes at 1 and 3 days of hydration, including a table with AFt amount at 1 and 3 days of hydration of cement pastes with gypsum and anhydrite. OPC compressive strength values are included for the sake of comparison.

To summarize, the dissolution rate of the different studied sulphate sources (gypsum, bassanite and anhydrite) is a key point to control the reactions during hydration of CSA cements, and hence the mechanical properties of the corresponding pastes and mortars, especially at 1 day of hydration. The ettringite contents (determined by RQPA and G-factor method) in combination with the setting time and plasticity of pastes and mortars justify the differences in compressive strength values. The results point out that anhydrite is the best sulphate source to be used in CSA mortars for engineering applications when high compressive strength values are needed at hydration time ≥ 3 days. However, if high strength values are demanded at earlier curing ages, gypsum is the best option. Conversely, CSA mortars prepared with bassanite had a dramatic effect onto the mechanical strength values and are not recommended unless the setting time could be delayed by the addition of the right type and amount of additives in the system.

ii) use of additives (retarders) in bassanite cement pastes and mortars

The objective of this final part was to control the hydration, including setting time, of CSA cements prepared with bassanite at w/CSA ratio of 0.50 and with the addition of different retarders: i) tartaric acid (TA); ii) nitrilotris(methylene)phosphonic acid (PA); and iii) polycarboxylate-based superplasticizer (PC). This work mainly includes rheological characterisation (very early ages), studies of the phase assemblage evolution, evolved heat and finally the compressive strength of the corresponding mortars.

In order to select the optimum amount of each additive, fresh pastes were rheologically characterized in the same way as explained before for CSA with gypsum (Figure 4.6.) It was observed that the optimum amount of each retarder (minimum of viscosity) were 0.15, 0.30 and 0.10 wt% of TA, PA and PC, respectively. With similar viscosity values, it should be selected the low amount of additive, because in a large scale use, the minimum amount of additive implies economic savings. However, in cement pastes with PA, similar viscosity value was also obtained with 0.20 wt% of PA additive; however the amount selected was 0.30 wt% due to the low rheopetic cycle (-625.3 and -79.17Pa·s^{-1}, respectively).

The evolution of viscosity with time of all pastes (different amounts and types of additive) was done at a shear rate of 4 s^{-1} according to observe the evolution. However, to continue the study were selected pastes with the optimum amount of each additive to study the differences between them (Figure 4.13.); Pastes with 0.10 wt% of PC presented the lowest viscosity during the first 30 minutes of hydration, at that time showed a sharp increase until 400 Pa·s, pastes with 0.30 wt% of PA showed the slowest rising of viscosity (around 100 minutes to gain 400 Pa·s) and cements with 0.15 wt % of TA viscosity increased quickly (20 min).

Paste	**Initial setting time**
B-paste	~20 min
B-paste; 0.10PC	~65 min
B-paste; 0.15TA	~65 min
B-paste; 0.30PA	~180 min

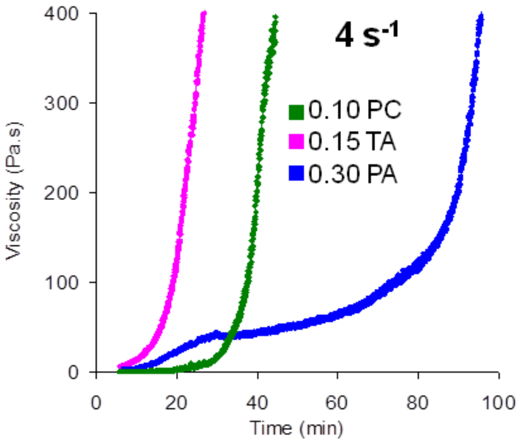


Figure 4.13. Viscosity vs. time curves at a shear rate of 4 s^{-1} for bassanite-cement pastes at w/c ratio of 0.50 (a) with the optimum amount of each additive in each case. Initial setting time of all the studied pastes at w/c=0.50 are included.

The use of additives increased the setting times. Figure 4.13. presents setting time values of B-pastes without and with the optimum amount of additive in each case; and it observes that they are increased by the retarded additions, as expected with the same trend as viscosity.

The phase assemblage was studied only at early age (1 and 7 days of hydration), because the aim of this study is to control the setting times and the early compressive strengths by adding different types of retarders. After 1 day of hydration similar amounts of AFt were formed in the three cases (~31 wt%) and, after 7 days, the formed amount were (40.1, 38.4 and 37.0 with PC, TA and PA, respectively). Thus, hydration was not affected by the retarder additions. To complete the hydration study conductivity and temperature measured of bassanite-cement pastes (w/c=0.50) with the optimum amount of each retarder were done, which decreased after a few minutes of hydration. Again, the trends of temperature and conductivity were in agreement with rheological behaviour (writing article).

In all cases, the addition of retarders improved the workability of pastes and mortars, delayed the setting time, affected the dissolution of ions (conductivity and temperature), and hence the ettringite formation and improved mechanical strengths. (see Figure 4.14). Bassanite mortars with compressible strength values comparable, and even better than gypsum or anhydrite mortars were obtained (compare Figure 4.12. and 4.14.) For instance, mortars with 0.10 wt% PC show the highest values of compressive strength at hydration time ≥ 3 days (75.1 MPa), however, at earlier ages (1 day), additions of 0.15 wt% TA or 0.30 wt% PA give the best results (45.8 and 44.0 MPa, respectively). These results pointed out PC as the best additive used in CSA mortars for engineering applications when high compressive strength values are needed at hydration time ≥ 3 days. However, if high strength values are demanded at earlier curing ages, TA or PA can be used.

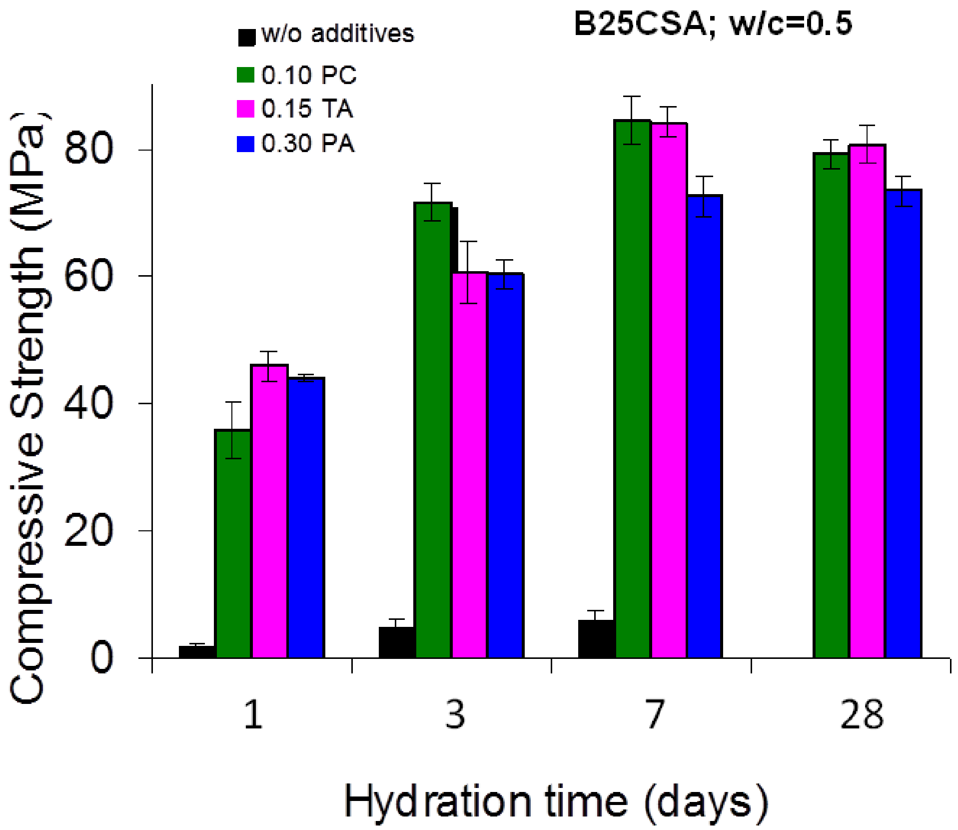


Figure 4.14. Compressive strength of bassanite-cement pastes.

5. Conclusions

5. Conclusions

In this PhD Thesis a reproducible methodology of processing and characterisation of hydrated CSA cement pastes has been established, including the quantification of ACn (Amorphous and Crystalline non-quantified) content that enable to understand and control the behaviour of these cement pastes during hydration. Moreover, the phase assemblage of CSA cement pastes has been correlated with the corresponding compressive strength values of their mortars at different curing times.

The main specific conclusions arisen from this PhD Thesis are numbered below:

1) The use of the optimum type and amount of additives improves the workability of cement pastes, allowing the use of lower w/c ratios, and consequently, higher compressive strength values are achieved (when compared to those mortars without any additive). Compressive strength values around 80 MPa at 7 days of hydration were obtained for mortars prepared with bassanite with 0.10 wt% of PC or 0.15 wt% of TA and w/CSA=0.50.

2) Although the stoichiometric amount of gypsum required to fully react with ye'elimite to form AFt in this CSA clinker is close to 30 wt%, the optimised amount of gypsum to prepare CSA cements has been determined to be 25 wt%. Lower amounts of gypsum (20 wt%) react completely and the remaining $C_4A_3\underline{S}$ is dissolved in water with the precipitation of calcium monosulphoaluminate hydrate (AFm). Conversely, greater amounts of gypsum (>30 wt%), leave unreacted gypsum without providing mechanical strength. Therefore, it has been demonstrated that the higher amounts of AFt (ettringite) in cements/mortars, the higher mechanical strengths (in the range of study).

3) The use of different sulphate sources is a key point to control the rate of the cement hydration. Every sulphate source (gypsum, bassanite or anhydrite) provides mortars with different setting times, as a consequence of their different rates of solubility. Bassanite solubility in water is high (0,88 g/100ml) thus, when added to cements/mortars it yields to short setting times (~20 min) producing heterogeneous mortars with low mechanical strengths (if retarders are not added). Anhydrite dissolves slowly (0,21 g/100ml) so, at 1 hydration-day (w/CSA=0.50), the amount of ettringite formed (~20 wt%) in anhydrite-pastes is lower than that in gypsum pastes (~26 wt%), producing mortars with lower compressive strengths. However, after 3 hydration-days, similar ettringite contents are produced but mechanical strengths of anhydrite-pastes are slightly higher than those for gypsum-pastes. This behaviour is mainly due to the higher plasticity of anhydrite-pastes to better accommodate the precipitation of ettringite. This higher plasticity is due to the slower rate of dissolution of anhydrite yielding longer setting times. In addition, it must be noted that Gypsum-w/c0.50 and Anhydrite-w/c0.50 mortars gave compressive strength values higher than those for OPC mortars at very early ages, i.e. 3 days.

4) The partial substitution of CSA cement by fly ash has two main effects on the mechanical properties of the mortars: i) filler and ii) dilution. The former slightly increases compressive strengths of the corresponding mortars, as observed in mortars with 15 wt% of FA at w/CSA=0.50 or 0.65. Contrarily, the latter predominates when 30 wt% of FA is added with negative effect in the mechanical strengths. For a fixed water/binder ratio, the compressive strengths of mortars decrease by increasing the amount of FA, mainly due to the higher water/CSA ratio, which causes higher porosity. The partial substitution of cement by 15 wt% of FA involves economic and environmental benefits. Moreover, the phase assemblage evolution during hydration is the same in the presence or in the

absence of FA, suggesting that durability is not compromised. A pozzolanic effect between FA and gibbsite could not be firmly established in this research.

5) At this point, we are able to obtain tailored CSA eco-cements and mortars for different applications through the control of the hydration of these cements prepared by adjusting different parameters: w/c ratio, type and amount of additives (superplasticizers or retarders), different sulphate sources and partial substitution of CSA by FA, with the consequent economic and environmental benefits.

5. Conclusions (Spanish version)

5. Conclusiones

En esta tesis doctoral se ha establecido una metodología reproducible para el procesado y caracterización de pastas hidratadas de cemento de sulfoaluminato de calcio (CSA), incluyendo la cuantificación de la materia amorfa y cristalina no cuantificada (ACn) que permite comprender y controlar el comportamiento de estos cementos durante el proceso de hidratación. Además, se ha correlacionado el ensamblaje de fases de las pastas de cemento CSA con los valores de resistencia a la compresión de los correspondientes morteros a diferentes edades de curado.

Las principales conclusiones específicas surgidas de esta tesis doctoral se detallan a continuación:

1) El uso del tipo y cantidad óptimos de aditivos mejora la trabajabilidad de las pastas de cemento, lo que permite el uso de una menor relación agua/cemento (a/c), alcanzándose valores de resistencia a la compresión más elevados (en comparación con los morteros sin ningún aditivo). Se obtuvieron morteros (preparados con basanita, con 0,10% en peso de PC ó 0,15% en peso de TA y con una relación agua/cemento=0,50) que presentaban valores de resistencia a compresión de ~80 MPa a los 7 días de hidratación.

2) Aunque la cantidad estequiométrica de yeso requerida en este clínker CSA para reaccionar con ye'elimita y formar AFt (etringita) es próxima a 30% en peso, la cantidad óptima de yeso ha resultado ser ~25% en peso. Menores cantidades de yeso (20% en peso) reaccionan completamente y la restante ye'elimita se disuelve en agua produciendo la precipitación de monosulfoaluminato de calcio hidratado (AFM). Por el contrario, mayores cantidades de yeso (>30% en peso), nos dejaría yeso sin reaccionar sin aportar resistencias mecánicas. Por lo que se ha demostrado

que los cementos/morteros con mayores cantidades de AFt desarrollan resistencias mecánicas superiores.

3) El uso de diferentes fuentes de sulfato es un punto clave en el control de la velocidad de la hidratación del cemento. Cada fuente de sulfato (yeso, basanita o anhidrita) proporciona un tiempo diferente de fraguado a los cementos/morteros, como consecuencia de su diferente tasa de solubilidad. La solubilidad de la basanita en el agua es la más alta (0,88 g/100ml), por lo que provoca tiempos de fraguado muy cortos (~20 min), y consecuentemente, morteros heterogéneos con resistencias mecánicas bajas (si no se añaden aditivos con acción retardante). Como la anhidrita es la que se disuelve más lentamente (0,21 g/100ml) de las tres, las pastas que la contienen presentan a 1 día de hidratación, ~20% en peso de AFt, lo que supone un valor más bajo que en las pastas con yeso, ~26% en peso de AFt; esto se transforma en menores resistencias a la compresión de los morteros con anhidrita después de un 1 de hidratación (a/c=0,50). Sin embargo, después de 3 días de hidratación, el contenido de etringita es similar en ambos casos, pero las resistencias mecánicas de los morteros con anhidrita son ligeramente superiores a las de los morteros con yeso. Este comportamiento se debe principalmente a la mayor plasticidad de las pastas con anhidrita, que permiten un mejor acomodamiento de la nueva etringita precipitada. Esta mayor plasticidad es debida a la menor velocidad de disolución de anhidrita y el mayor tiempo de fraguado producido. Además, hay que señalar que los morteros de yeso-a/c=0,50 y de la anhidrita-a/c=0,50 dieron valores de resistencia a la compresión superiores a los de los morteros de OPC a edades muy tempranas (3 días).

4) La sustitución parcial del cemento CSA por cenizas volantes tiene dos efectos principales sobre las propiedades mecánicas de los morteros: i) efecto de relleno y ii) efecto de dilución. El primero aumenta ligeramente las resistencias a la compresión de los correspondientes morteros, como es el caso de la sustitución del

15% en peso por cenizas volantes en a/c=0,50 o 0,65. Por el contrario, este último efecto predomina cuando el cemento es sustituido por 30% en peso de cenizas volantes con un efecto negativo en las resistencias mecánicas. Para una relación agua/sólido fija, las resistencias a la compresión de los morteros disminuyen al aumentar la cantidad de cenizas volantes, debido principalmente a la relación a/c más alta, lo que provoca mayor porosidad. La sustitución parcial del cemento en un 15% en peso por cenizas volantes implica beneficios económicos y ambientales. Por otra parte, la evolución del ensamblaje de fases durante la hidratación es el mismo en presencia o en ausencia de cenizas volantes, lo que sugiere que la durabilidad no se vea comprometida. Finalmente, el efecto puzolánico entre cenizas volantes y gibbsita no pudo ser firmemente establecido en esta investigación.

5) En este punto, estamos en condiciones de obtener eco-cementos CSA y morteros "a la carta" con diferentes propiedades para diferentes aplicaciones, a través del control de la hidratación de estos cementos mediante el ajuste de los diferentes parámetros: relación agua/cemento, tipo y cantidad de aditivos (superplastificantes o retardantes), diferentes fuentes de sulfato y la sustitución parcial de cemento por cenizas volantes, con los consecuentes beneficios económicos y ambientales.

6. References

6. References

A

Abdul-Maula S and Older I (1992), "SO_3-rich Portland cements: synthesis and strength development", *Mat Res Soc Symp Proceedings,* 245, 315-320.

Adolfsson D, Menad N, Viggh E and Bjorkman B (2007), "Hydraulic properties of sulphoaluminate belite cement based on steelmaking slags", *Adv Cem Res,* 19, 133-138.

Alaoui A, Feraille A, Steckmeyer A and Le Roy R (2007), "New cements for sustainable development", *Proceedings of 12th International Congress on the Chemistry of Cement*, Montreal, Canada.

Alesiani M, Pirazzoli I, Maraviglia B and Canonico F (2008), "NMR and XRD study on calcium sulfoaluminate cement", *Appl Magn Reson,* 35, 33-41.

Ali M M, Gopal S and Handoo S K (1994), "Studies on the formation kinetics of calcium sulphoaluminate", *Cem Concr Res,* 24(4), 715-720.

Allmann R (1977), "Refinement of the hybrid layer structure $[Ca_2Al(OH)_6]\cdot0.5(SO_4)\cdot3H_2O$", Neues Jahrb Mineral Monatsh, 136-144.

Álvarez-Pinazo G, Cuesta A, García-Maté M, Santacruz I, De la Torre A G, León-Reina L and Aranda M A G (2012), "Rietveld quantitative phase analysis of Yeelimite-containing cements", *Cem Concr Res*, 42, 960-971.

Álvarez-Pinazo G, Cuesta A, García-Maté M, Santacruz I, Losilla E R, Sanfélix S G, Fauth F, Aranda M A G and De la Torre A G (2014), "In-situ early-age hydration study of sulfobelite cements by synchrotron powder diffraction", *Cem Concr Res,* 56, 12-19.

Álvarez-Pinazo G, Santacruz I, León-Reina L, Aranda M A G and De La Torre A G (2013), "Hydration reactions and mechanical strength developments of iron-rich sulfobelite eco-cements" *Ind Eng Chem Res,* 52(47), 16606-16614.

Ambroise J, Georgin J F, Peysson S and Péra J (2009), "Influence of polyether polyol on the hydration and engineering properties of calcium sulphoaluminate cement", *Cem Concr Comp*, 31, 474-482.

Andac M and Glasser F P (1999), "Pore solution composition of calcium sulphoaluminate cement", *Adv Cem Res*, 11, 23-26.

Aranda M A G, Cuberos A J M, Cuesta A, Alvarez-Pinazo G, De la Torre A G, Schollbach K, Pöllmann H (2011), “Hydrating behaviour of activated belite sulfoaluminate cements”, *Proceedings of the 13th International Congress on the Chemistry of Cement*, Madrid, Spain.

Aranda M A G, De la Torre A G and León-Reina L (2012), “Rietveld quantitative phase analysis of OPC clinkers, cements and hydration products”, *Rev Mineral Geochem,* 74, 169-209.

Aranda, M A G and De la Torre A G (2013), “Sulfoaluminate cement” in Eco-efficient Concrete, Pacheco-Torgal F, Jalali S, Labrincha J and John V M (Eds.), Woodhead Publishing, Cambridge, 488-522.

Aranda M A G, De la Torre A G and León-Reina L (2015), “Powder diffraction characterisation of cements”, International Tables for Crystallography. Volume H-Powder Diffraction, in press.

Arjunan P, Silsbee M R and Roy D M (1999), “Sulfoaluminate-belite cement from low-calcium fly ash and sulfur-rich and other industrial by-products”, *Cem Concr Res*, 29, 1305-1311.

Ataie F F and Riding K A (2014), “Use of bioethanol byproduct for supplementary cementitious material production”, *Constr Build Mater*, 51, 89-96.

B

Banfill P F G (2006), “Rheology of fresh cement and concrete”, Rheology Reviews, 61-130.

Barnes P and Bensted J (2002), “Structure and performance of cements”, in Taylor and Francis, Spon Press, London, 565.

Barcelo L, Kline J, Walenta G and Gartner E (2014), “Cement and carbon emissions”, *Mater Struct*, 47, 1055-1065.

Benarchid M Y, Diouri A, Boukhari A, Aride J, Rogez J and Castanet R (2004), “Elaboration and thermal study of iron-phosphorus-substituted dicalcium silicate phase”, *Cem Concr Res*, 34, 1873-1879.

Bensted J (1979), “Some hydration studies of α-dicalcium silicate”, *Cem Concr Res*, 9, 97-101.

Bentur A and Ish-Shalom M (1974), "Properties of Type K expansive cement and pure components", *Cem Concr Res*, 4, 709-721.

Beretka J, De Vito B, Santoro L, Sherman N and Valenti G L (1993), "Hydraulic behavior of calcium sulfoaluminate-based cements derived from industrial process wastes", *Cem Concr Res*, 23, 1205-1214.

Beretka J, Marroccoli M, Sherman N and Valenti G L (1996), "The influence of $C_4A_3\underline{S}$ content and w/s ratio on the performance of calcium sulfoaluminate-based cements", *Cem Concr Res*, 26, 1673-1681.

Berger S, Cau Dit Coumes C, Le Bescop P and Damidot D (2011a), "Influence of a thermal cycle at early age on the hydration of calcium sulphoaluminate cements with variable gypsum contents", *Cem Concr Res*, 41, 149-160.

Berger S, Cau Dit Coumes C, Le Bescop P, and Damidot D (2011b), "Stabilization of $ZnCl_2$-containing wastes using calcium sulfoaluminate cement: Cement hydration, strength development and volume stability", *J Haz Mat*, 194, 256-267.

Berger S, Cau Dit Coumes C, Le Bescop P, and Damidot D (2011c), "Stabilization of $ZnCl_2$-containing wastes using calcium sulfoaluminate cement: Leaching behaviour of the solidified waste form, mechanisms of zinc retention", *J Haz Mat*, 194, 268-276.

Berger S, Cau Dit Coumes C, Le Bescop P, Aouad G and Damidot D (2011d), "Leaching of calcium sulfoaluminate cement-based materials: experimental investigation and modelling", *Proceedings of the 13th international Congress on the Chemistry of Cement*, Madrid, Spain.

Bernardo G, Telesca A and Valenti G L (2006), "A porosimetric study of calcium sulfoaluminate cement pastes cured at early ages", *Cem Concr Comp*, 36, 1042-1047.

Bessy G I (1938), "The calcium aluminate and silicate hydrates", *Symp on the Chem of Cements*, Stockholm, Sweden.

Bish D L and Howard S A (1988), "Quantitative phase analysis using the Rietveld method", *J Appl Crystallogr*, 21, 86-91.

Bishop M and Barron A R (2006), "Cement hydration inhibition with sucrose, tartaric acid and lignosulfonate: analytical and spectroscopic study", *Ind Eng Chem Res*, 45, 7042-7049.

Bishop M, Bott S G and Barron A R (2003), “A new mechanism for cement hydration inhibition: solid-state chemistry of calcium nitrilotris(methylene)triphosphonate”, *Chem Mater,* 15, 3074-3088.

Bizzozero J, Gosselin C and Scrivener K L (2014), “Expansion mechanisms in calcium aluminate and sulfoaluminate systems with calcium sulfate”, *Cem Concr Res,* 56, 190-202.

Björnstom J and Chandra S (2003), “Effect of superplasticizers on the rheological properties of cements”, *Mat Struct*, 36, 685-692.

Blezard R G (2004), “The history of calcareous cements”. In Lea´s Chemistry of Cement and Concrete, published by Arnold, London UK, p. 1.

Bullerjahn F, Schmitt D and Ben Haha M (2014), “Effect of raw mix design and of clinkering process on the formation and mineralogical composition of (ternesite) belite calcium sulphoaluminate ferrite clinker”, *Cem Concr Res*, 2014, 59, 87-95.

Buzzi L, Canonico F and Schäffel P (2011), “Investigation on High-Performance Concrete based on Calcium Sulfoaluminate cement”, *Proceedings of the 13th International Congress on the Chemistry of Cement,* Madrid, Spain.

C

Calos N J, Kennard C H L, Whittaker A K and Davis R L (1995), “Structure of calcium aluminate sulfate $Ca_4Al_6O_{16}S$”, *J Solid State Chem,* 119, 1-7.

Canonico F, Bernardo G, Buzzi L, Paris M, Telesca A and Valenti G L (2007), “Microstructural investigations on hydrated high-performance cements based on calcium sulfoaluminate”, *Proceedings of the 12th International Congress of Cement Chemistry,* Montreal, Canada.

Catti M, Gazzoni G and Ivaldi G (1984), “Order-disorder in the α'-$(Ca,Sr)_2SiO_4$ solid solution: a structural and statistical-thermodynamic analysis”, *Acta Cryst,* B40, 537-544.

Cau Dit Coumes C, Courtois S, Peysson S, Ambroise J and Péra J (2009), “Calcium sulfoaluminate cement blended with OPC: a potential binder to encapsulate low-level radioactive slurries of complex chemistry”, *Cem Concr Res,* 39, 740-747.

Champenois J B, Dit Coumes C C, Poulesquen A, Le Bescop P and Damidot D (2013), “Beneficial use of a cell coupling rheometry, conductimetry, and calorimetry to investigate the early age hydration of calcium sulfoaluminate cement” *Rheol Acta*, 52, 177-187.

Chan C J, Kriven W M and Young J F (1988), “Analytical electron microscopic studies of doped dicalcium silicates”, *J Am Ceram Soc,* 71, 713-719.

Chang W, Li H, Wei M, Zhu Z, Zhang J and Pei M (2009), “Effects of polycarboxylic acid based superplasticiser on properties of sulphoaluminate cement”, *Mater Res Innovations*, 13, 7-10.

Chen I A, Hargis C W and Juenger M C G (2012), “Understanding expansion in calcium sulfoaluminate-belite cements”, *Cem Concr Res,* 42, 51-60.

Chen Y L, Lin C J, Ko M S, Lai Y C and Chang J E (2011), “Characterization of mortars from belite-rich clinkers produced from inorganic wastes”, *Cem Concr Com*, 33, 261-266.

Cheung J, Jeknavorian A, Roberts L and Siva D (2011), “Impact of admixtures on the hydration kinetics of Portland cement”, *Cem Concr Res*, 41, 1289-1309.

Chong J S, Christiansen E B and Bear A D (1971), “Rheology of concentratedfields” *J Appl Polym Sci*, 15, 2007-2021.

Cline J P, Von Dree R B, Winburn R, Stephens P W and Filliben J J (2011), “Addressing the amorphous content issue in quantitative phase analysis: the certification of NIST standard reference material 676a”, *Acta Crystallogr*, A67, 357-367.

Coussot P (2005), “Rheometry of Pastes, Suspensions and Granular Materials”, New York, John Wiley & Sons.

Cuberos A J M, De la Torre A G, Álvarez-Pinazo G, Martín-Sedeño M C, Schollbach K, Pöllmann H and Aranda M A G (2010), “Active Iron-Rich Belite Sulfoaluminate Cements: Clinkering and Hydration”, *Env Sci Tech*, 44, 6855-6862.

Cuberos A J M (2011), “Caracterización de cementos belíticos de sulfoaluminato de calcio” PhD Thesis University of Málaga, Spain.

Cuesta A, Losilla E R, Aranda M A G, Sanz J and De la Torre A G (2012), “Reactive belite stabilization mechanisms by boron-bearing dopants”, *Cem Concr Res*, 42, 598-606.

Cuesta A, De la Torre A G, Losilla E R, Peterson V K, Rejmak P, Ayuela A, Frontera C and Aranda M A G (2013), "Structure, Atomistic Simulations, and Phase Transition of
Stoichiometric Yeelimite", *Chem Mater*, 25, 1680-1687.

Cuesta A, Álvarez-Pinazo G, Sanfélix S G, Peral I, Aranda M G A and De la Torre A G (2014a), "Hydration mechanisms of two polymorphs of synthetic ye'elimite", *Cem Concr Res*, 63, 127-136.

Cuesta A, Aranda M A G, Sanz J, De la Torre A G and Losilla E R (2014b), "Mechanism of stabilization of dicalcium silicate solid solution with aluminium", *Dalton Trans*, 43, 2176-2182.

Cuesta A, De la Torre A G, Losilla E R, Santacruz I and Aranda M A G (2014c), "Pseudo-cubic crystal structure and phase transition in doped ye'elimite", *Cryst Growth Des*, 14, 5158−5163

Cuesta A, Álvarez-Pinazo G, García-Maté M, Santacruz I, Aranda M A G, De la Torre A G and León-Reina L (2014d), "Rietveld quantitative phase analysis with Molybdenum radiation" Powder Diff. in press.

D

Damtoft J S, Lukasik J, Herfort D, Sorrentino D and Gartner E M (2008), "Sustainable development and climate change initiatives", *Cem Concr Res,* 38(2), 115-127.

De la Torre A G, Bruque S and Aranda M A G (2001), "Rietveld quantitative amorphous content analysis", *J Appl Crystallogr*, 34, 196-202

De la Torre A G, Morsli K, Zahir M. and Aranda M A G (2007), "In-situ synchrotron powder diffraction study of active belite clinkers", *J Appl Cryst*, 27, 892-900.

De la Torre A G, Cuberos A J M, Álvarez-Pinazo G, Cuesta A and Aranda M A G (2011a), "In situ powder diffraction study of belite sulfoaluminate clinkering", *J Synch Rad*, 18, 506-514.

De la Torre A G, Cuberos A J M, Álvarez-Pinazo G, Cuesta A and Aranda M A G (2011b), "In-Situ Clinkering Study of Belite Sulfoaluminate Clinkers by Synchrotron X-Ray Powder Diffraction", *Proceedings of the 13th International Congress on the Chemistry of Cement,* Madrid, Spain.

Deng M and Tang M (1994), “Formation and expansion of ettringite crystals”, *Cem Concr Res*, 24, 119-126.

De Weerdt K, Ben Haha M, Le Saoût G, Kjellsen K O, Justnes H and Lothenbach B (2011), “Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash” *Cem Concr Res*, 41, 279-291.

Dinnebier R E and Billinge S J L (Eds.) (2008), Powder Diffraction: Theory and Practice, Royal Society of Chemistry, Publishing, Cambridge.

Dollase W A (1986), “Correction of intensities for preferred orientation in powder diffractometry: application of the March model”, *J Appl Crystallogr*, 19, 267-272.

F

Fernandez-Jimenez A, Monzo M, Vicent M, Barba A and Palomo A (2008), “Alkaline activation of metakaolin–fly ash mixtures: Obtain of Zeoceramics and Zeocements”, *Micropor Mesopor Mat*, 108, 41-49.

Fierens P and Tirlocq J (1983), “Nature and concentration effect of stabilizing elements of Beta-dicalcium silicate on its hydration rate”, *Cem Concr Res*, 13, 267-276.

François M, Renaudin G and Evrad O (1998), “A cementitious compound with composition $3CaO\cdot Al_2O_3\cdot CaCO_3\cdot 11H_2O$”, *Acta Cryst*, C54, 1214-1217.

Fukuda K and Ito S (1999), “Improvement in reactivity and grindability of belite-Rich cement by remelting reaction”, *J Am Cer Soc*, 82, 2177-2180.

Fukuda K, Wakamatsu N and Ito S (2001), “Improvement in hydration reactivity of α-phase belite by remelting reaction”, *J Am Ceram Soc*, 84(3), 639-641.

Fu X, Yang C, Liu Z, Tao W, Hou W and Wu X (2003), “Studies on effects of activators on properties and mechanism of hydration of sulphoaluminate cement”, *Cem Concr Res*, 33, 317-324.

G

Gartner E (2004), “Industrially interesting approaches to low-CO2 cement”, *Cem Concr Res*, 34, 1489-1498.

Gartner E and Li G (2006), “High-belite sulfoaluminate clinker: fabrication process and binder preparation”, World Patent Application WO2006/018569 A2.

Gartner E and Macphee D E (2011), “A physico-chemical basis for novel cementitious binders”, *Cem Concr Res*, 41, 736-749.

Gastaldi D, Boccaleri E, Canonico F and Bianchi M (2007), “The use of Raman spectroscopy as a versatile characterization tool for calcium sulphoaluminate cements: a compositional and hydration study”, *J Mater Sci*, 42, 8426-8432.

Gastaldi D, Canonico F, Capelli L, Bianchi M, Pace M L, Telesca A and Valenti G L (2011), “Hydraulic Behaviour of Calcium Sulfoaluminate Cement alone and in Mixture with Portland Cement”, *Proceedings of the 13th International Congress on the Chemistry of Cement*, Madrid, Spain.

Georgin J F, Ambroise J, Péra J and Reynouard J M (2008), “Development of self-leveling screed based on calcium sulfoaluminate cement: Modelling of curling due to drying”, *Cem Concr Com*, 30, 769-778.

Ghosh S N, Rao P B, Paul A K and Raina K J (1979), “The chemistry of the dicalcium silicate mineral”, *J Mater Sci*, 14, 1554-1566.

Gielen D and Tanaka K, (2006), "Energy efficiency and CO_2 emission reduction potentials and policies in the cement industry: towards a plan of action", *Proceedings of the IEA/WBCSD Workshop on Energy Efficiency and* CO_2 *Emission Reduction Potentials and Policies in the Cement Industry*, Paris, France.

Glasser F P and Zhang L (2001), “High-performance cement matrices based on calcium sulphoaluminate-belite compositions”, *Cem Concr Res*, 31, 1881-1886.

Gomá F (1979), “El cemento Portland y otros aglomerantes”. Editores Técnicos Asociados, Barcelona, Spain.

Gualtieri A F, Riva V, Bresciani A, Maretti S, Tamburini M and Viani A (2014), “Accuracy in quantitative phase analysis of mixtures with large amorphous contents. The case of stoneware ceramics and bricks”, *J Appl Cryst*, 47, 835-846.

Guo X, Shi H, Hub W and Wub K (2014), “Durability and microstructure of CSA cement-based materials from MSWI fly ash”, *Cem Concr Com*, 46, 26–31.

H

Hall C and Scrivener K L (1998), “Oilwell cement clinkers: X-ray microanalysis and phase composition”, *Advn Cem Bas Mat*, 7, 28-38.

Halstead P and Moore A E J (1962), “The composition and crystallography of an anhydrous calciumaluminosulphate occurring in expanding cement”, *Appl Chem*, 12, 413-417.

Hanehara S and Yamada K (2008), “Rheology and early age properties of cement systems”, *Cem Concr Res*, 21, 175-195.

Hargis C W, Telesca A and Monteiro P J M (2014), “Calcium sulfoaluminate (Ye'elimite) hydration in the presence of gypsum, calcite, and vaterite”, *Cem Concr Res,* 56, 12-19.

Hayes M and Godfrey I H (2007), “Development of the use of alternative cements for the treatment of intermediate level waste”, *Proceedings of the Waste Management Symposium*, Tucson, Arizona.

Herrick J, Scrivener K L and Pratt P L (1992), “The development of microstructure in calcium sulfoaluminate expansive cement”, *Mat Res Soc Symp Proceedings*, Pittsburgh, USA, 277-282.

Hill R J and Howard C J (1987), “Quantitative phase analysis from neutron powder diffraction data using the Rietveld method”, *J Appl Crystallogr*, 20, 467-474.

I

Il’inets A M and Bikbau M Y (1990), “Structural mechanism of polymorphic transformations of dicalcium silicate, Ca_2SiO_4. Part II. Refinement of crystal structure of high temperature α'_L modification of dicalcium silicate Ca_2SiO_4”, *Sov Phys Crystallogr*, 35, 54-56.

Ioannou S, Reig L, Paine K and Quillin K (2014), “Properties of a ternary calcium sulfoaluminate–calcium sulfate–fly ash cement”, *Cem Concr Res,* 56, 75-83.

J

Jackson P J (2004), “Portland Cement: Classification and Manufacture”. In Lea´s Chemistry of Cement and Concrete, published by Arnold, London UK, p. 2.

Janotka I and Krajci L (1999), “An experimental study on the upgrade of sulfoaluminate-belite cement systems by blending with Portland cement”, *Adv Cem Res*, 11, 35-41.

Janotka I, Krajci L, Ray A and Mojumdar S C (2003), “The hydration phase and pore structure formation in the blends of sulfoaluminate-belite cement with Portland cement”, *Cem Concr Res,* 33, 489-497.

Janotka I, Krajci U and Mojumdar S C (2007), “Performance of sulphoaluminate-belite cement with high $C_4A_3\$$ content”, *Cer Silik,* 51, 74-81.

Jansen D, Stabler CH, Goetz-Neunhoeffer F, Dittrich S and Neubauer J (2011a), “Does ordinary Portland cement contain amorphous phase? A quantitative study using an external standard method”, *Powder Diffrn*, 26, 31-38.

Jansen D, Bergold S T, Goetz-Neunhoeffer F and Neubauer J (2011b), “The hydration of alite: a time-resolved quantitative X-ray diffraction approach using the G-factor method compared with heat release”, *J Appl Crystallogr,* 44, 895-901.

Jelenic I, Bezjak A and Bujan M (1978), “Hydration of B_2O_3-stabilized α’- and β-modifications of dicalcium silicate”, *Cem Concr Res,* 8, 173-180.

Jost K H, Ziemer B and Seydel R (1977), “Retermination of the structure of β-dicalcium silicate”, *Acta Cryst*, B33, 1696-1700.

Juenger M and Chen I (2011), “Composition-Property Relationships in Calcium Sulfoaluminate Cements”, *Proceedings of the 13th International Congress on the Chemistry of Cement,* Madrid, Spain.

Juenger M C G, Winnefeld F, Provis J L and Ideker J H (2011), “Advances in alternative cementitious binders”, *Cem Concr Res,* 41, 1232-1243.

Juilland P, Gallucci E, Flatt R and Scrivener K (2010), “Dissolution theory applied to the induction period in alite hydration”, *Cem Concr Res*, 40, 831-844.

K

Kantro D L and Weise C H (1979), “Hydration of various beta-dicalcium silicate preparations”, *J Am Cer Soc*, 62, 621-626.

Katsioti M, Tsakiridis P E, Leonardou-Agatzini S and Oustadakis P (2006), “Examination of the jarosite–alunite precipitate addition in the raw meal for the production of sulfoaluminate cement clinker”, *J Haz Mat,* B131, 187-194.

Klaus S R, Neubauer J and Goetz-Neunhoeffer F (2013), Hydration kinetics of CA_2 and CA-Investigations performed on a synthetic calcium aluminate cement”, *Cem Concr Res*, 43, 62-69.

Klein A (1963), “Calciumaluminosulfate and expansive cements containing same”, US Patent 3155526.

Klein A (1966), “Expansive and Shrinkage-Compensated Cements”, US Patent 3251701.

Kurdowski W and Thiel A (1981), “On the role of free calcium oxide in expansive cements”, *Cem Concr Res,* 11, 29-40.

Kurokawa D, Takeda S, Colas M, Asaka T, Thomas P and Fukuda K (2014), “Phase transformation of $Ca_4[Al_6O_{12}]SO_4$ and its disordered crystal structure at 1073K”, *J Solid State Chem,* 215, 265-270.

Kuryatnyk T, Angulski-Da-Luz C, Ambroise J and Pera J (2008), “Valorization of phosphogypsum as hydraulic binder”, *J Haz Mat*, 160, 681-687.

Kuryatnyk T, Chabannet M, Ambroise J and Pera J (2010), “Leaching behaviour of mixtures containing plaster of Paris and calcium sulphoaluminate clinker”, *Cem Concr Res*, 40, 1149-1156.

L

Larson A C and Von Dreele R B (2000), General structure analysis system
(GSAS). Los
Alamos national laboratory report LAUR, 86-748.

Laźniewska-Piekarczyk B (2014), “The methodology for assessing the impact of new generation superplasticizers on air content in self-compacting concrete”, Constr Build Mater, 53, 488-502.

Le Saoût G, Lothenbach B, Hori A, Higuchi T and Winnefeld F (2013), “Hydration of Portland cement with additions of calcium sulfoaluminates”, *Cem Concr Res,* 43, 81-94.

Levita G, Marchetti A, Gallone G, Princigallo A and Guerrini GL (2000), “Electrical properties of fluidified Portland cement mixes in the early stage of hydration”, *Cem Concr Res,* 30, 923-930.

Liao Y, Wei X, Li G (2011), “Early hydration of calcium sulfoaluminate cement through electrical resistivity measurement and microstructure investigations”, *Constr Build Mater,* 25, 1572–1579

Li H, Agrawal D K, Cheng J and Silsbee M R (2001), "Microwave sintering of sulphoaluminate cement with utility wastes", *Cem Concr Res,* 31, 1257-1261.

Li G S, Walenta G and Gartner E M (2007a), "Formation and hydration of low-CO_2 cements based on belite, calcium sulfoaluminate and calcium aluminoferrite", *Proceedings of the 12th International Congress of the Cements Chemistry*, Montreal, Canada.

Li J, Ma H and Zhao H (2007b), "Preparation of Sulphoaluminate-alite Composite Mineralogical Phase Cement Clinker from High Alumina Fly Ash", *Key Eng Mat,* 334-335, 421-424.

Li X, Zhang Y, Shen X, Wang Q and Pan Z (2014), "Kinetics of calcium sulphoaluminate formation from tricalcium aluminate, calcium sulfate and calcium oxide" *Cem Concr Res*, 55, 79-87.

Lili R, Xiaocun L, Tao Q, Lian L, Deli Z and Yanjun L (2009), "Influence of MnO_2 on the Burnability and Mineral Fornnation of Alite-sulphoaluminate Cement Clinker" *Sil Ind*, 74, 183-187.

Lingchao L, Jun C, Xin C, Hanxing L and Runzhang Y (2005), "Study on a cementing system taking alite-calcium barium sulphoaluminate as main minerals", *J Mat Sci*, 40, 4035-4038.

Liu X and Li Y (2005), "Effect of MgO on the composition and properties of alite-sulphoaluminate cement", *Cem Concr Res,* 35, 1685-1687.

Liu X C, Li B L, Qi T, Liu X L and Li Y J (2009), "Effect of TiO_2 on mineral formation and properties of alite-sulphoaluminate cement", *Mat Res Innov*, 13(2), 92-97.

Lothenbach B, Scrivener K L and Hooton R D (2011), "Supplementary cementitious materials", *Cem Concr Res*, 41, 1244-1246.

Lura P, Winnefeld F and Klemm S (2010), "Simultaneous measurements of heat of hydration and chemical shrinkage on hardening cement pastes", *J Therm Anal Calorim*, 101, 925-932.

Luz C A, Rocha J C, Cheriaf M and Pera J (2006), "Use of sulfoaluminate cement and bottom ash in the solidification/stabilization of galvanic sludge", *J Haz Mater*, B136, 837-845.

Luz C A, Rocha J C, Cheriaf M and Pera J (2009), “Valorization of galvanic sludge in sulfoaluminate cement”, *Const Build Mat*, 23, 595-601.

M

Ma S, Shen X, Gong X and Zhong B (2006), “Influence of CuO on the formation and coexistence of $3CaO \cdot SiO_2$ and $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ minerals”, *Cem Concr Res*, 36, 1784-1787.

Ma B, Li X, Shen X, Mao Y and Huang H (2014a), “Enhancing the addition of fly ash from thermal power plants in activated high belite sulphoaluminate cement”, *Const Build Mat*, 52, 261-266.

Ma B, Ma M, Shen X, Li X and Wu X (2014b), “Compatibility between a polycarboxylate superplasticizer and the belite-rich sulfoaluminate cement: Setting time and the hydration properties”, *Const Build Mat*, 51, 47-54.

Madsen I C, Scarlett N V Y and Kern A (2011), “Description and survey of methodologies for the determination of amorphous content via X-ray powder diffraction”, Z Kristallogr, 226, 944-955.

Marchi M and Costa U (2011), “Influence of the Calcium Sulfate and W/C Ratio on the Hydration of Calcium Sulfoaluminate Cement”, *Proceedings of the 13th International Congress on the Chemistry of Cement*, Madrid, Spain.

Martín-Sedeño M C, Cuberos A J M, De la Torre A G, Álvarez-Pinazo G, Ordónez L M, Gateshki M and Aranda M A G (2010), “Aluminum-rich belite sulfoaluminate cements: clinkering and early age hydration”, *Cem Concr Res*, 40, 359-369.

Matkovic B, Carin V, Gacesa T, Halle R, Jelenic I and Young J F (1981), “Influence of $BaSO_4$ on the Formation and Hydration Properties of Calcium Silicates: I, Doped Dicalcuim Silicates”, *Am Ceram Soc Bull*, 60, 825-829.

McCaffrey R (2002), “Climate change and the cement industry”, *Global Cement and Lime Magazine Environmental Special Issue*, 15-19.

McCarter W J and Currant P N (1984), “The electrical response characteristics of setting cement paste”, *Mag Concr Res*, 36, 42-49.

Mechling J, Lecomte A, Roux A and Le Rolland B (2013), “Sulfoaluminate cement behaviours in carbon dioxide, warm and moist environments”, *Adv Cem Res*, 26(1), 52-61.

Mehta P K (1973), “Mechanism of expansion associated with ettringite formation”, *Cem Concr Res,* 3, 1-6.

Mehta P K and Hu F (1975), “Further evidence for expansion of ettringite by water absorption”, *J Am Ceram Soc*, 61, 179-181.

Mehta P K (1977), “High iron oxide hydraulic cement”, US patent 4036657.

Mehta P K and Wang S (1982), “Expansion of ettringite by water absorption”, *Cem Concr Res,* 12, 121-122.

Mehta P K and Monteiro J M P (2006), “Concrete: microstructure, properties, and materials”, 3rd edition, New York, McGraw-Hill.

Meller N, Hall C, Jupe A C, Colston S L, Jacques S D M, Barnes P and Phipps J (2004), “The paste hydration of brownmillerite with and without gypsum: a time resolved synchrotron diffraction study at 30, 70, 100 and 150 ºC”, *J Mater Chem,* 14, 428-435.

Michel M, Georgin J F, Ambroise J and Péra J (2011), “The influence of gypsum ratio on the mechanical performance of slag cement accelerated by calcium sulfoaluminate cement”, *Cons Build Mat,* 25, 1298-1304.

Midgley C M (1952), “The crystal structure of β-dicalcium silicate”, *Acta Cryst,* 5, 307-312.

Moore P B (1973), “Bracelets and Pinwheels: A topological-Geometrical approach to the calcium orthosilicate and alkali sulfate structures”, *Am Mineral*, 58, 32-42.

Moreno R (2005), “Reología de suspensiones cerámicas. Editorial: Consejo Superior de Investigaciones Científicas (Spanish Council for Scientific Research)”, *In Spanish*.

Morin V, Walenta G and Gartner E, Termkhajornkit P, Baco I and Casabonne J M (2011), “Hydration of a Belite-Calcium Sulfoaluminate- Ferrite cement: AetherTM”, *Proceedings of the 13th International Congress on the Chemistry of Cement,* Madrid, Spain.

Morsli K, De la Torre A G, Stöber S, Cuberos A J M, Zahir M and Aranda M A G (2007a), “Quantitative Phase Analysis of Laboratory Active Belite Clinkers by Synchrotron Powder Diffraction”, *J Amer Cer Soc*, 90, 3205-3212.

Morsli K, De la Torre A G, Zahir M and Aranda, M A G (2007b), “Mineralogical Phase Analysis of Alkali and Sulfate Bearing Belite Rich Laboratory Clinkers”, *Cem Concr Res*, 37, 639-646.

Morsy M S (1999), “Effect of temperature on electrical conductivity of blended cement pastes”, *Cem Concr Res*, 29, 603-606.

Mumme W G, Hill R J, Bushnell-Wye G and Segnit E R (1995), “Rietveld structure refinement, crystal chemistry and calculated powder diffraction data for the polymorphs of dicalcium silicate and related phases”, *N Jb Miner Abh*, 169, 35-68.

Mumme W, Cranswick L and Chakoumakos B (1996), “Rietveld crystal structure refinements from high temperature neutron powder diffraction data for the polymorphs of dicalcium silicate”, *N Jb Miner Abh*, 170, 171-188.

N

Nettleship I, Slavick K G, Kim Y J and Kriven W M (1992), “Phase transformation in dicalcium silicate: I, Fabrication and phase stability of fine-grained β-phase”, *J Am Cer Soc*, 75, 2400-2406.

Neville A M (1995), Properties of concrete, 4th edition, Essex, Pearson.

O

O´Connor B H abd Raven M D (1988), “Application of the Rietveld refinement procedure in assaying powdered mixtures”, *Powder Diffr*, 3, 2-6.

O’Daniel H and Tscheischwili L (1942), “Zur struktur von γ-Ca_2SiO_4 und Na_2BeF_4”, *Z Kristallogr*, 104, 124-141.

Odler I (2000), ”Special inorganic cements” in Taylor and Francis Publisher, cap 4, 69-74.

Odler I and Zhang H (1996), “Investigations on high SO_3 Portland clinkers and cements I. Clinker synthesis and cement preparation”, *Cem Concr Res*, 26, 1307-1313.

Ogawa K and Roy D M (1981), “$C_4A_3\underline{S}$ hydration, ettringite formation and its expansive mechanism: I. Expansion; ettringite stability”, *Cem Concr Res*, 11, 741-750.

P

Pace M L, Telesca A, Marroccoli M and Valenti G L (2011), “Use of Industrial Byproducts as Alumina Sources for the Synthesis of Calcium Sulfoaluminate Cements”, *Env Sci Tech*, 45, 6124-6128.

Paglia C, Wombacher F and Bohni H (2001), “The influence of alkali-free and alkaline shotcrete accelerators within cement systems I. Characterization of the setting behavior”, *Cem Concr Res*, 31, 913-918.

Palacios M, Houst Y F, Bowen P and Puertas F (2009), “Adsorpion of superplasticizer admixtures on alkali-activated slag pastes”, *Cem Concr Res*, 39, 670-677.

Palou M, Majling J, Dovál M, Kozanková J and Mojumdar S C (2005), “Formation and stability of crystallohydrates in the non-equilibrium system during hydration of SAB cements”, *Cer Silik*, 49, 230-236.

Pang X, Boontheung P and Boul P J (2014), “Dynamic retarder exchange as a trigger for Portland cement hydration”, *Cem Concr Res*, 63, 20-28.

Park C K (2001), “Phase transformation and hydration of dicalcium silicate containing stabilizers”, *J Cer Soc Jap*, 109, 380-386.

Paul G, Boccaleri E, Buzzi L, Canonico F and Gastaldi F (2015), “Friedel's salt formation in sulfoaluminate cements: A combined XRD and ^{27}Al MAS NMR study”, *Cem Concr Re*, 67, 93-102.

Pecharsky V and Zavalij P (2005), “Fundamentals of Powder Diffraction and Structural Characterization of Materials”, Springer, New York.

Pelletier L, Winnefeld F and Lothenbach B (2010), “The ternary system Portland cement–calcium sulphoaluminate clinker–anhydrite: Hydration mechanism and mortar properties”, *Cem Concr Comp* , 32, 497-507.

Pelletier-Chaignat L, Winnefeld F, Lothenbach B, Le Saout G, Müller C J and Famy C (2011), “Influence of the calcium sulphate source on the hydration mechanism of portland cement–calcium sulphoaluminate clinker–calcium sulphate binders”, *Cem Concr Comp*, 33, 551-561.

Pelletier-Chaignat L, Winnefeld F, Lothenbach B and Müller C J (2012), “Beneficial use of limestone filler with calcium sulphoaluminate cement”, *Cons Build Mat*, 26, 619-627.

Péra J, Ambroise J, Holard E and Beauvent G (2003), “Influence of the type of calcium sulfate on the properties of calcium sulfoaluminate cement”, *Proceedings of the 11th International Congress on the Chemistry of Cement*, Durban, South Africa, 1129-1135.

Pera J and Ambroise J (2004), “New applications of calcium sulfoaluminate cement”, *Cem Concr Res*, 34, 671-676.

Pérez-Bravo R, Álvarez-Pinazo G, Compana J M, Santacruz I, Losilla E R, Bruque S and De la Torre A G (2014), “Alite sulfoaluminate clinker: Rietveld mineralogical and SEM-EDX analysis”, *Adv Cem Res*, 26(1), 10-20.

Peysson S, Pera J and Chabannet M (2005), “Immobilization of heavy metals by calcium sulfoaluminate cement”, *Cem Concr Res*, 35, 2261-2270.

Phair J W (2006), “Green chemistry for sustainable cement production and use”, *Green Chem*, 8, 763-780.

Pliego-Cuervo Y B and Glasser F P (1979), “The role of sulfates in cement clinkering: subsolidus phase relations in the system CaO-Al_2O_3-SiO_2-SO_3”, *Cem Concr Res*, 9, 51-56.

Pritts M and Daugherty K E (1976), “The effect on stabilizing agents on the hydration rate of β-C_2S”, *Cem Concr Res*, 6, 783-796.

Popescu C D, Muntean M and Sharp J H (2003), “Industrial Trial Production of Low Energy Belite Cement”, *Cem Concr Comp*, 25, 689-693.

Prudêncio Jr L R (1998), “Accelerating admixtures for shotcrete”, *Cem Concr Comp*, 20, 213–219.

Puertas F, Blanco-Varela M T and Giménez-Molina S (1995), “Kinetics of the thermal decomposition of $C_4A_3\underline{S}$ in air”, *Cem Concr Res*, 25, 572-580.

Q

Qian G R, Shi J, Cao Y L, Xu Y F and Chui P C (2008), “Properties of MSW fly ash–calcium sulfoaluminate cement matrix and stabilization/solidification on heavy metals”, *J Haz Mat*, 152, 196-203.

Quillin K (2001), “Performance of belite–sulfoaluminate cements”, *Cem Concr Res*, 31, 1341–1349.

R

Renaudin G, Kubel F, Rivera J P and Francois M (1999), "Structural phase transition and high temperature phase structure of Friedels salt, $3(CaO)(Al_2O_3)(CaCl_2)\cdot 10(H_2O)$", *Cem Concr Res*, 29, 1937-1942.

Regourd M and Guinier A (1974), "The Crystal Chemistry of the Constituents of Portland Cement Clinker", *VI Inter Symp on the Chem of Cements*, Moscow, Russia.

Rietveld H M (1967), "Line profiles of neutron powder-diffraction peaks for structure refinement", *Acta Crystallogr*, 22, 151-152.

Rietveld H M (1969), "A profile refinement method for nuclear and magnetic structures", *J Appl Crystallogr*, 2, 65-71.

Rietveld H M (2010), "The Rietveld method", *Conference at the 10th Spanish Summer School on the Rietveld Method*, Castellon, Spain.

Rinaldi R, Sacerdoti M and Passaglia E (1990), "Straetlingite: crystal structure, chemistry and a reexamination of its polytype vertumnite", *Eur J Mineral*, 2, 841-849.

Roussel N (Ed.) (2012), "Understanding the rheology of concrete", Woodhead Publishing Limited.

S

Saalfeld H and Depmeier W (1972), "Silicon-free compounds with sodalite structure", *Kristall Technik*, 7, 229-233.

Sahu S, Havlica J, Tomková V and Majling J (1991), "Hydration behaviour of sulphoaluminate belite cement in the presence of various calcium sulphates", *Thermochim Acta*, 175, 45-52.

Sahu S and Majling J (1993), "Phase compatibility in the system $CaO–SiO_2–Al2O_3–Fe_2O_3–SO_3$ referred to sulphoaluminate belite cement clinker", *Cem Concr Res*, 23, 1331-1339.

Sahu S and Majling J (1994), "Preparation of sulphoaluminate belite cement from fly ash", *Cem Concr Res*, 24, 1065-1072.

Salem T M (2002), “Electrical conductivity and rheological properties of ordinary Portland cement–silica fume and calcium hydroxide–silica fume pastes”, *Cem Concr Res*, 32, 1473-1481.

Scarlett N V Y and Madsen I C (2006), “Quantification of phases with partial or no known crystal structures”, *Powder Diffr*, 21, 278-284.

Schneider M, Romer M, Tschudin M and Bolio H (2011), “Sustainable cement production-present and future”, *Cem Concr Res*, 41, 642-650.

Schramm G (Ed.) (1984), “Introducción a la viscosimetría práctica”, Haake, Karlsruhe, Alemania.

Schreyer M, Guo L, Tjahjono M and Garland M (2011), “Three approaches to total quantitative phase analysis of organic mixtures using an external standard”, *J Appl Crystallogr*, 44, 17-24.

Schulte C, Mader H and Wittmann F H (1978), “Electric Conductivity of Hardened Cement Paste at Different Moisture Contents”, *Cem Concr Res*, 8, 359-368.

Scrivener K L and Kirkpatrick R J (2008), “Innovation in use and research on cementitious material”, *Cem Concr Res*, 38, 128-136.

Seluck N, Soner I and Seluck E (2010), “Synthesis of special cement with fluidised bed combustion ashes”, *Adv Cem Res*, 22, 107-113.

Senff L, Castela A, Hajjaji W, Hotza D and Labrincha J A (2011), “Formulations of sulfobelite cement through design of experiments”, *Cons Build Mat*, 25, 3410-3416.

Sharp J H, Lawrence C D and Yang R (1999), “Calcium sulphoaluminate cements–Low-energy cements, special cements or what?”, *Adv Cem Res*, 11, 3-13.

Shen Y, Qian J, Chai J and Fan Y (2014), “Calcium sulphoaluminate cements made with phosphogypsum:Production issues and material properties”, *Cem Concr Comp*, 48, 67-74.

Singh M and Pradip P C K (2008), “Preparation of calcium sulphoaluminate cement using fertiliser plant wastes”, *J Haz Mat*, 157, 106-113.

Smith D K, Johnson G G, Scheible A, Wims A M, Johnson J L and Ullrnann G (1987), “Quantitative X-ray powder diffraction method using the full diffraction pattern”, *Powder Diffr*, 2, 73-77.

Snellings R, Mertens G and Elsen J (2012), “Supplementary cementitious materials”, *Rev Mineral Geochem*, 74, 211-278.

Snellings R, Bazzoni A and Scrivener K (2014), “The existence of amorphous phase in Portland cements: Physical factors affecting Rietveld quantitative phase analysis”, *Cem Concr Res*, 59, 139-146.

Sokol E V, Kokh S N, Vapnik Y, Thiéry V and Korzhova1 S A (2014), “Natural analogous of belite sulfoaluminate cement clinkers from Negev Desert, Israel”, *Am Mineral*, 99, 1471-1487.

Stickel J J and Powell R L (2005), “Fluid mechanics and rheology of dense suspensions”, *Ann Rev Fluid Mech*, 37, 129-149.

Suherman P M, Riessen A V, O'Connor B, Li D, Bolton D and Fairhurst H (2002), “Determination of amorphous phase levels in Portland cement clinker”, *Powder Diffr*, 17, 178-185.

Sun Q, Li J and Wang J (2011), “Effect of borate concentration on solidification of radioactive wastes by different cements”, *Nucl Engin Design*, 241, 4341-4345.

T

Tattersall G H and Banfill P F G (First published 1993), ”The Rheology of Fresh Concrete” Editorial: Pitman Advanced Publishing Program.

Taylor H F W (1997), “Cement Chemistry”, Thomas Telford. London.

Taylor J C and Zhu R (1992), “Simultaneous use of observed and calculated standard profiles in quantitative XRD analysis of minerals by the multiphase Rietveld method: the determination of pseudorutile in mineral and products”, *Powder Diffr*, 7, 152-161.

Telesca A, Marroccoli M, Pace M L and Valenti G L (2011), “Calcium Sulfoaluminate Cements Obtained from Bauxite-Free Raw Mixes”, *Proceedings of the 13th International Congress on the Chemistry of Cement*, Madrid, Spain.

Telesca A, Marroccoli M, Pace M L, Tomasulo M, Valenti G L and Monteiro P J M (2014), “A hydration study of various calcium sulfoaluminate cements”, *Cem Concr Comp*, 53, 233-238.

Termkhajornkit P, Nawa T and Kurumisawa K (2006), “Effect of water curing conditions on the hydration degree and compressive strengths of fly ash–cement paste”, *Cem Concr Comp*, 28, 781-789.

Thomas N L and Birchall J D (1983), “The retarding action of sugars on cement hydration”, *Cem Concr Res*, 13, 830-842.

Toby B H (2001), “EXPGUI, a graphical user interface for GSAS”, *J Appl Crystallogr*, 34, 210-213.

Topcu I B, Uygunoglu T and Hocaoglu I (2012), “Electrical conductivity of setting cement paste with different mineral admixtures”, *Constr Build Mater*, 28, 414-420.

Touzo B, Scrivener K L and Glasser F P (2013), “Phase compositions and equilibria in the $CaO–Al_2O_3–Fe_2O_3–SO_3$ system, for assemblages containing ye'elimite and ferrite $Ca_2(Al,Fe)O_5$”, *Cem Concr Res*, 54, 77-86.

U

Uchikawa H, Sawaki D and Hanehara S (1995), “Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement paste”, *Cem Concr Res*, 25(2), 353-364.

Udagawa S, Urabe K, Takada K and Natsume M (1979), “Studies on the dusting of Ca_2SiO_4. The crystal structure of α'_L-Ca_2SiO_4”, *Cem Assoc Jpn Rev, Gen Meet, Tech Sess*, 33, 35-38.

Udagawa S, Urabe K, Natsume M and Yano T (1980), “Refinement of the crystal-structure of γ-Ca_2SiO_4”, *Cem Concr Res*, 10(2), 139-144.

U.S. Geological Survey, Mineral Commodity Summaries. January 2014.

V

Valenti G L, Marroccoli M, Montagnaro F, Nobili M and Telesca A (2007), “Synthesis, hydration properties and environmental friendly features of calcium sulfoaluminate cements”, *Proceedings of the 12th International Congress of Cement Chemistry*, Montreal, Canada.

Vázquez T and Gutiérrez-Jiménez J P (2001), “XV Curso de Estudios Mayores de la Construcción” CEMCO. IETCC, CSIC, Madrid.

Viani A, Gualtieri A F (2013), "Recycling the product of thermal transformation of cement-asbestos for the preparation of calcium sulfoaluminate clinker", *J Hazard Mater*, 260, 813-818.

Viswanathan V N, Raina S J and Chatterjee A K (1978), "An exploratory investigation on Porsal cement", *World Cem Tech*, 109-118.

W

Walenta G and Comparet C (2011), "New Cements and Innovative Binder Technologies BCSAF cements-recent developments", ECRA-Barcelona-2011. Presentation available at http://www.aether-cement.eu/press-room/publications/aether-cement-ecra-barcelona-presentation-2011-05-05.html.

Wang Y G, Ye H Q, Kuo K H, Feng X J, Lao G L and Long S Z (1990), "Electron diffraction and HREM studies of the new phase and superstructures in $Ca_4Al_6SO_{16}$", *J Mater Sci*, 25, 5147-5156.

Wang S, Ji S, Liu Y and Hu K (1986), "Effect of alkali on the expansive properties of sulfoaluminate cement pastes", *Proceedings of the 8th International Congress on the Chemistry of Cement*, Rio De Janeiro, Brazil.

Wei X and Li Z (2006), "Early hydration process of Portland cement paste by electrical measurement", *J Mater Civ Eng*, 18, 99-105.

Wesselsky A and Jensen O M (2009), "Synthesis of pure Portland cement phases", *Cem Concr Res*, 39, 973-980.

Westphal T, Fullmann T and Pollmann H (2009), "Rietveld quantification of amorphous portions with internal standard-Mathematical consequences of the experimental approach", *Powder Diffr*, 24, 239-243.

Westphal T, Walenta G, Giménez M, Bermejo E, Füllmann T, Scrivener K and Pöllmann H (2002), "Characterisation of cementitious materials-PART III", *Inter cem rev*, 47-51

Whitfield P S and Mitchell L D (2003), "Quantitative Rietveld analysis of the amorphous content in cements and clinkers", *J Mater Sci*, 38, 4415-4421.

Whittington H W, McCart J and Forde M C (1981), "The conduction of electricity through concrete", *Mag Concr Res*, 33, 48-60.

Wieland E, Lothenbach B, Glaus M.A, Thoenen T and Schwyn B (2014), "Influence of superplasticizers on the long-term properties of cement pastes and possible impact on radionuclide uptake in a cement-based repository for radioactive waste" Appl Geochem, *In press*.

Winnefeld F and Barlag S (2009), "Influence of calcium sulfate and calcium hydroxide on the hydration of calcium sulfoaluminate clinker", *Zkg Int*, 12, 42-53.

Winnefeld F and Barlag S (2010), "Calorimetric and thermogravimetric study on the influence of calcium sulfate on the hydration of ye´elimite", *J Therm Anal Calorim*, 101, 949-957.

Winnefeld F and Lothenbach B (2010), "Hydration of calcium sulfoaluminate cements - Experimental findings and thermodynamic modeling", *Cem Concr Res*, 40, 1239-1247.

Winnefeld F, Ben-Haha M and Lothenbach B (2011), "Hydration mechanisms of calcium sulfoaluminate cements assessed by scanning electron microscopy and thermodynamic modelling", *Proceedings of the 13th International Congress on the Chemistry of Cement*, Madrid, Spain.

Wolter A (2005), "Belite cements and low energy clinker", *Cem Inter*, 3, 106-117.

Wu K, Shi H and Guo X (2011), "Utilization of municipal solid waste incineration fly ash for sulfoaluminate cement clinker production", *Waste Manag*, 31, 2001-2008.

X

Xu Q and Stark J (2005), "Quantification of cement hydration when using an alkali-free setting accelerator", *Zkg Int*, 58, 68-79.

Y

Yang L, Yan Y, Hu Z and Xie X (2013), "Utilization of phosphate fertilizer industry waste for belite–ferroaluminate cement production", *Const Build Mat*, 38, 8-13.

Yanjun L, Xiaocun L and Lili R (2007), "Study of tbe Properties of Compounded Alite-sulphoaluminate Cement and Portland Cement", *Silic Ind*, 72, 15-18.

Z

Zhang D, Ju B Z, Zhang S F, He L and Yang J Z (2002), "The study on the dispersing mechanism of starch sulfonate as a water-reducing agent for cement", *Cem Concr Res,* 32(2), 187-98.

Zhang H and Odler I (1996), "Investigations on high SO_3 Portland clinkers and cements II. Properties of cements", *Cem Concr Res,* 26, 1315-1324.

Zhang J and Scherer G W (2011), "Comparison of methods for arresting hydration of cement", *Cem Concr Res,* 41, 1024-1036.

Zhang L and Glasser F P (2000), "Critical examination of drying damage to cement pastes", *Adv Cem Res,* 12, 79-88.

Zhang L and Glasser F P (2002), "Hydration of calcium sulfoaluminate cement at less than 24 h", *Adv Cem Res* 14, 141-155.

Zhang L and Glasser F P (2005), "Investigation of the microstructure and carbonation of CSA-based concretes removed from service", *Cem Concr Res* 35, 2252-2260.

Zhang L, Su M Z and Wang Y M (1999), "Development of the use of sulfo-and ferro-aluminate cements in China", *Adv Cem Res,* 11, 15-21.

Zhang P, Chen Y, Shi L, Zhang G and Huang W W J (1992), "The crystal structure of $C_4A_3\underline{S}$", *Proceedings of the 9th International Congress on the Chemistry of Cement,* New Delhi, India.

Zhou Q, Milestone N B and Hayes M (2006), "An alternative to Portland cement for waste encapsulation-the calcium sulfoaluminate cement system", *J Haz Mater,* 136, 120-129.

Ziemer B, Altrichter B and Jesenak V (1984), "Effect of SO_3 on formation and hydraulic reactivity of belite", *Cem Concr Res,* 14, 686-692.

Zivica V (2000), "Properties of blended sulfoaluminate belite cement", *Const Build Mat,* 14, 433-437.

Zivica V (2001), "Possibility of the modification of the properties of sulfoaluminate belite cement by its blending", *Const Build Mat,* 45, 24-30.

Annex

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Rietveld quantitative phase analysis of Yeelimite-containing cements

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ABSTRACT

Yeelimite-containing cements are attracting attention for their tailored properties. Calcium sulfoaluminate, CSA, cements have high contents of Yeelimite and they are used for special applications. Belite calcium sulfoaluminate, BCSA or sulfobelite, cements have high contents of belite and intermediate contents of Yeelimite, and they may become an alternative to OPC. Here, we report Rietveld quantitative phase analyses for three commercially available CSA clinkers, one CSA cement, and two laboratory-prepared iron-rich BCSA clinkers. The crystalline phases are reported and quantified. Selective dissolutions are employed for BCSA clinkers to firmly establish their phases. Finally, the overall unaccounted contents (amorphous plus crystalline not quantified) have been determined by two approaches: i) external standard procedure (G-method) with reflection data; ii) internal standard procedure (spiking method with ZnO) with transmission data. The overall unaccounted contents for CSA clinkers were ~10 wt.%. Conversely, the unaccounted contents for BCSA clinkers were higher, ~25 wt.%.

1. Introduction

Calcium sulfoaluminate (CSA) cements have been applied worldwide from the 60s as expansive binders mixed with Portland cements [1]. These cements are characterized by containing high amounts of Yeelimite, also called Klein's salt or tetracalcium trialuminate sulfate ($C_4A_3\underline{S}$). Hereafter, cement nomenclature will be used, i.e. $C=CaO$, $S=SiO_2$, $A=Al_2O_3$, $F=Fe_2O_3$, $M=MgO$, $\underline{S}=SO_3$, $\underline{C}=CO_2$, $H=H_2O$, $K=K_2O$ and $N=Na_2O$. Therefore, $C_4A_3\underline{S}$ corresponds to $Ca_4Al_6O_{12}(SO_4)$. During the 70s, CSA cements were introduced into the Chinese market as high performance and dimensionally stable cementitious matrices developed by the China Building Materials Academy [2]. In Europe, the use of CSA cements is strongly limited by the lack of standards concerning special cements derived from non-Portland clinkers. Nevertheless, their manufacture has recently been started by several companies. The main use of these CSA cements, or blends with Portland cements, is for quick repairs and pre-cast products or floor concrete applications.

Moreover, Yeelimite-containing cements have become highly popular over the last few years for research. The driving force for these investigations is the much lower CO_2 emissions in their manufacture when compared to those of Portland cement production due to the following main reasons [3,4]: i) Yeelimite releases during its synthesis only a third part of the CO_2 released by the production of alite, ii) firing temperature is about 200 °C lower than that of OPC clinker, iii) various industrial by-products can be used in the kiln feed, and iv) Yeelimite-containing clinkers are easier to grind than OPC clinkers. The improvement of cement performances and the reduction of the environmental impact related to its manufacture are most likely the main areas of innovation for the cement industry [5]. It must be highlighted that CSA cements may have important special applications such radioactive element encapsulation in high-density cement pastes [6]. Other interesting properties of Yeelimite-containing cements are high early strengths, short setting times, low solution alkalinity as well as high impermeability and chemical resistance against several aggressive media [7].

However, while the composition of Portland cement is defined by long-standing codes and standards, there is no corresponding compositional framework for Yeelimite-containing cements. These clinkers may show very variable phase assemblage. The raw mix composition can be based on conventional raw materials (limestone, clay, bauxite and iron ores); in addition, industrial by-products and wastes can also be added [8,9]. Yeelimite-containing cements could be classified according to their $C_4A_3\underline{S}$ contents as:

I) Calcium sulfo-aluminate (CSA) cements which would refer to those with high $C_4A_3\underline{S}$ contents. They may be prepared from CSA clinkers containing $C_4A_3\underline{S}$ as the main phase ranging between 50 and 90 wt.% [10]. The calcium sulfate addition is very important as it may profoundly affect the properties of the resulting binder [11–13]. The calcium sulfate source and content have to be customized for a given application. These

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In-situ early-age hydration study of sulfobelite cements by synchrotron powder diffraction

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ABSTRACT

Eco-friendly belite calcium sulfoaluminate (BCSA) cement hydration behavior is not yet well understood. Here, we report an *in-situ* synchrotron X-ray powder diffraction study for the first hours of hydration of BCSA cements. Rietveld quantitative phase analysis has been used to establish the degree of reaction (α). The hydration of a mixture of ye'elimite and gypsum revealed that ettringite formation (α ~70% at 50 h) is limited by ye'elimite dissolution. Two laboratory-prepared BCSA cements were also studied: non-active-BCSA and active-BCSA cements, with β- and α'_H-belite as main phases, respectively. Ye'elimite, in the non-active-BCSA system, dissolves at higher pace (α ~25% at 1 h) than in the active-BCSA one (α ~10% at 1 h), with differences in the crystallization of ettringite (α ~30% and α ~5%, respectively). This behavior has strongly affected subsequent belite and ferrite reactivities, yielding stratlingite and other layered phases in non-active-BCSA. The dissolution and crystallization processes are reported and discussed in detail.

1. Introduction

Concrete is the most used artificial material, 6 km^3/year or more than 2.5 tones per person yearly. This is due to many interesting features including low price, high versatility, remarkable change in mechanical properties during setting and chemical durability. The hydration of cements, to yield concrete, is a very complex process in which some crystalline phases are dissolved in free water. Pore solution becomes saturated in some ions, and after oversaturation, some crystalline and amorphous hydrated phases start to precipitate [1,2]. These processes are responsible for the development of a given microstructure (type, amount and distribution of the constituent phases, usually with chemical substitutions on the crystalline phases, and porous distribution) which is the fundamental link between chemical processes and final properties/performances. Many factors may affect the equilibrium between hydrous phases, pore solution, gel/amorphous phases and clinker phases, and their kinetics of dissolution and formation. Because of that, it is essential to understand (and at later stage to control) the hydration processes, in particular within the first few hours of hydration, named in the field as early hydration [2].

However, the complexity and heterogeneity of cementitious materials make difficult the understanding of the process–microstructure–properties relationship. Furthermore, there are only a few rapid, reliable and accurate techniques to quantify the amounts of the different phases present in the hydrated cements (pastes), including amorphous contents and porous (micro) structure [3–6]. Due to these difficulties, the details of the hydration process of cements are still not completely clarified, even when the cement chemistry is well known in its most important features, as it is the case for ordinary Portland cement (OPC) [2]. These problems are enhanced for novel cementitious materials. Scientific community is searching for new cements with improved performances, such as high strengths and good workability of their corresponding concretes and/or environmentally friendly binders [7]. However, prior to the reliable use of any new binder, the hydration chemistry and durability of the mortars and concretes must be profoundly studied and characterized, as the safety and wealth of people are very much related to building industry.

Belite calcium sulfoaluminate [8], BCSA or sulfobelite, cements are considered environmentally friendly building materials, as their production may have up to 35% lower CO_2 footprint than OPC fabrication. They are prepared by mixing the clinker with different amounts of a calcium sulfate set regulator such as gypsum, bassanite or anhydrite. Hereafter cement nomenclature will be used: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\underline{S} = SO_3$, $T = TiO_2$ and $H = H_2O$. BCSA cements are based on belite (C_2S), ye'elimite (also called Klein's salt or tetracalcium trialuminate sulfate ($C_4A_3\underline{S}$)) and other minor phases, such as ferrite (C_4AF) [9–13] or calcium aluminates ($C_{12}A_7$) [14] and calcium sulfate ($C\underline{S}H_x$) as set retarder. The hydration of BCSA cements strongly depends on the amount and reactivity of the added calcium sulfate [15] and the presence of minor phases. Most of the hydration heat is released within the first 12–24 h of hydration [11,16,17]. The

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TECHNICAL ARTICLE

Rietveld quantitative phase analysis with molybdenum radiation

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Building materials are very complex samples of worldwide importance; hence quantitative knowledge of their mineralogical composition is necessary to predict performances. Rietveld quantitative phase analysis (RQPA) allows a direct measurement of the crystalline phase contents of cements. We highlight in this paper the use of laboratory X-ray powder diffraction (LXRPD) employing high-energy radiation, molybdenum (Mo), for attaining the RQPA of cements. Firstly, we evaluate the accuracy of RQPA employing a commercial calcium sulfoaluminate clinker with gypsum. In addition to Mo$K\alpha_1$ and Mo$K\alpha_{1,2}$ radiations, Cu and synchrotron patterns are also analyzed for the sake of comparison. Secondly, the assessment of the accuracy of RQPA results obtained using different radiations (synchrotron, Mo, and Cu) and geometries (reflection and transmission) is performed by analyzing two well-known commercial samples. As expected, for LXRPD data, accuracy in the RQPA results improves as the irradiated volume increases. Finally, three very complex aged hydrated cements have been analyzed using Mo$K\alpha_1$-LXRPD and Synchrotron-XRPD. The main overall outcome of this work is the benefit for RQPA of using strictly monochromatic Mo$K\alpha_1$ radiation. Best laboratory results arise from Mo$K\alpha_1$ data as the effective tested volume is much increased but peak overlapping is not swelled. © *2014 International Centre for Diffraction Data*. [doi:10.1017/S0885715614000785]

Key words: Mo and Cu radiations, synchrotron radiation, irradiated volume, cement, accuracy

I. INTRODUCTION

In a standard laboratory instrument, the X-rays are produced in a sealed-tube source, in the same way as they were produced in the original tube discovered by W. C. Rontgen in 1895, where electrons accelerated by a potential difference of up to 60 kV bombard a metal anode inside a vacuum tube. Such sources differ only in the intensity of the radiation produced. The most common target elements are Cu for powder diffraction and molybdenum (Mo) for single-crystal studies. Alternative radiations, both with lower (Cr, Fe, and Co) and higher (Ag and W) energies, are employed for very special applications. For routine powder diffraction work, a Cu tube is the most common choice, giving the wavelength 1.5406 Å. Heavier elements are believed to give too short wavelengths for most practical use in the laboratory, as they exacerbate the peak overlapping, although they become important for total scattering, pair distribution function (PDF) studies and in order to avoid fluorescence from samples containing elements excited by Cu radiation (Dinnebier and Billinge, 2008). On the other hand, the advantages of high-energy penetrating laboratory X-ray sources are: (i) larger irradiated volumes, (ii) lower absorption effects, and (iii) more accessible Bragg reflections. However, to keep the angular resolution in powder diffraction is a key point since high-energy patterns are squeezed and therefore, if the appropriate optic elements are not present, peak overlap may become an important drawback.

For powder diffraction-based quantitative phase analysis procedures, it is generally accepted that the peak intensities need to be measured to an accuracy of about ±1–2% relative (Dinnebier and Billinge, 2008). The ability to achieve this goal is strongly influenced by the size of the crystallites in the sample and their number contributing to the Debye–Scherrer cone (Smith, 2001). Reproducible diffraction intensities in zero-dimensional (0D) or 1D detectors require smooth cones which are obtained from samples containing small crystallite size(s) and high-enough number of crystallites per phase. Elton and Salt (1996) estimated the number of crystallites diffracting in a sample. Fluctuations in peak intensity between replicate samples arise largely from statistical variation in the number of particles contributing to the diffraction process. It was shown that small changes to the instrumental and sample configurations can significantly improve the sample particle statistics. For a given sample, several methods can be used to increase the number of crystallites contributing to the diffraction pattern, including: (i) rotate the sample about the normal to the sample surface for a flat plate sample or the sample axis for a capillary sample; (ii) oscillate the sample about the incident angle axis, this motion removes the exact Bragg–Brentano $\theta/2\theta$ relationship between sample and receiving slit and may lead to aberrations in the peak intensities; (iii) repack the sample, recollect, and reanalyze the diffraction data, averaging the results from each analysis will produce more meaningful parameter values, (iv) reduce the average crystallite size(s) by milling (Buhrke *et al.*, 1998), however,

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