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Effect of ZnO on the reactivity of cementitious systems

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Lausanne, le 24 septembre 2022 Andrea Teixeira

Abstract

One of the biggest driving forces in cement research today is the mitigation of the CO_2 emissions caused by its production. A potential solution to reduce the environmental impact is to replace cement with supplementary cementitious materials (SCMs). This replacement results in low strength at early ages because they are slow to react. The incorporation of minor elements has shown the potential to improve cement reactivity. A few percent of ZnO in C_3S causes a significant increase in reactivity. This effect was related to the incorporation of zinc into the C-S-H structure, which increases its needle length. This research investigates the effect of ZnO in more realistic systems such as alite, C_3A-polyclinker, and C_4AF-polyclinker. The positive effects observed in C_3S are translated in the alite system, but differences were found in the polyclinkers, which have a prolonged induction period. This resulted due concentration of zinc in the interstitial material and a small amount of zinc in alite phase. An amorphous phase was identified in the C_3A polyclinker; it is believed to react rapidly with water, releasing Zn ions into the solution, which delays the reaction of alite. The addition of more gypsum controls the reaction of this phase, and thus the induction period is shortened.

This work explores the possibilities of retaining Zn in alite to enhance the reactivity of more realistic cementitious systems. The cooling rate was critical, as a slow cooling rate promoted more Zn in the alite, less amorphous, and hence, an enhancement in the hydration of C_3A-polyclinker doped with ZnO. The recalcination of this system did not affect the hydration of alite but increased the amount of crystalline C_3A, which reacted faster. Thus, the amorphous phase was related to an aluminate phase. Moreover, a C_4AF-polyclinker and a system with a lower amount of interstitial material were investigated. The results showed a higher Zn concentration in alite but also extended induction periods. This was associated with the free ZnO and the amorphous content. Even when the hydration was delayed, the height of the alite peak increased with Zn doping, probably due to the incorporation of Zn into the C-S-H observed in pure C_3S.

In addition, the interaction between sulfates and zinc in the alite system doped with ZnO was investigated. Severe retardation was observed, and the reason is proposed to be the formation of amorphous Zn compound. The presence of aluminum, ettringite formation, or an amorphous layer were discarded as the cause of the retardation.

Keywords

Clinker, zinc oxide, reactivity, clinkerization, cooling rate, amorphous content, microstructure, hydration.

Résumé

Actuellement, une des motivations principales de la recherche dans le domaine du ciment est l'atténuation des émissions de CO_2 causées par sa production. Une solution potentielle pour réduire l'impact environnemental consiste à remplacer le ciment par des matériaux cimentaires supplémentaires (MCS). Ce remplacement se traduit par une faible résistance aux premiers âges car ils sont lents à réagir. L'incorporation d'éléments mineurs a montré qu'il était possible d'améliorer la réactivité du ciment. Quelques pourcentages de ZnO dans le C_3S provoquent une augmentation significative de la réactivité. Cet effet était lié à l'incorporation du zinc dans la structure C-S-H, qui augmente la longueur de ses aiguilles. Cette recherche étudie l'effet du ZnO dans des systèmes plus réalistes tels que l'alite, le C_3A-polyclinker et le C_4AF-polyclinker. Les effets positifs observés dans C_3S sont traduits dans le système alite, mais des différences ont été trouvées dans les polyclinkers, qui ont une période d'induction prolongée. Il en résulte une concentration de zinc dans les phases interstitielles et une faible quantité de zinc dans la phase alite. Une phase amorphe a été identifiée dans le polyclinker C_3A ; on pense qu'elle réagit rapidement avec l'eau, libérant des ions Zn dans la solution, ce qui retarde la réaction de l'alite. L'ajout de plus de gypse permet de contrôler la réaction de cette phase, et donc de raccourcir la période d'induction.

Ce travail explore les possibilités de retenir le Zn dans l'alite pour améliorer la réactivité de systèmes cimentaires plus réalistes. Le taux de refroidissement était critique, car un taux de refroidissement lent a favorisé plus de Zn dans l'alite, moins amorphe, et donc, une amélioration de l'hydratation du C_3A-polyclinker dopé au ZnO. La recalcination de ce système n'a pas affecté l'hydratation de l'alite mais a augmenté la quantité de C_3A cristallin, qui a réagi plus rapidement. Ainsi, la phase amorphe était liée à une phase aluminate. De plus, un polycyclinker C_4AF et un système avec une plus faible quantité de phase interstitielle ont été étudiés. Les résultats ont montré une concentration plus élevée de Zn dans l'alite mais aussi des périodes d'induction prolongées. Ceci était associé au ZnO libre et au contenu amorphe. Même lorsque l'hydratation a été retardée, la hauteur du pic de l'alite a augmenté avec le dopage Zn, probablement en raison de l'incorporation de Zn dans le C-S-H observé dans le C_3S pur.

De plus, l'interaction entre les sulfates et le zinc dans le système alite dopé avec ZnO a été étudiée. Un retard sévère a été observé, et la raison est proposée comme étant la formation d'un composé Zn amorphe. La présence d'aluminium, la formation d'ettringite, ou une couche amorphe ont été écartées comme cause du retard.

Mots-clés

Clinker, oxyde de zinc, réactivité, clinkérisation, vitesse de refroidissement, contenu amorphe, microstructure, hydratation.

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Chapter 1 Introduction

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1.1 Cement industry: climate crisis and alternatives

Cement is one of the most important construction materials. It is a substance that, when mixed with water, hardens and binds objects together. It is made mainly from the most abundant elements on the earth's crust. Therefore, its manufacture and development can be scaled worldwide as the raw materials are widely available. Cement is the key ingredient of concrete, combined with aggregates of different sizes and water. Concrete is the most produced material by humankind and, together with steel reinforcement, forms the basis for modern structural engineering.

Environmentally, the CO_2 emissions by mass of concrete production are lower compared to other materials. However, its massive production means that the overall environmental impact is significant. The cement industry contributes to up to 8% of anthropogenic CO_2 emissions [1].

No other material can compete with concrete because of its low economic cost, the raw materials are widely spread, no special formation is needed for its use, and it brings the essential mechanical and durability properties for the large infrastructures needed nowadays, plus its versatility makes it a unique material in terms of architectural and artistic design. Therefore, cement and concrete will continue to be the leading construction materials for the upcoming years, in which the population is expected to increase and, consequently, the housing demand. Thus, it is crucial to reduce its environmental impact.

The use of renewable energies might help to reduce CO_2 emissions but not solve the problem. Most of the CO_2 associated with cement and concrete production comes from the breakdown of limestone, which is around 80% of the raw material to produce cement. Hence, the most efficient approach to reduce concrete's impact is to replace part of the cement with supplementary cementitious materials (SCMs). These materials are by-products or wastes from other industries with hydraulic or pozzolanic properties. Currently, the average substitution level is not higher than 30% [2], and the most common SCMs are granulated blast furnace slag from the production of iron and steel and fly ash waste from burning coal to produce electricity.

Even though the substitution by SCMs is the most promising strategy, it has two main limitations. First, the availability of these materials, fly ash comes from coal-fired power stations, slag from steel industry blast furnaces, and these industries are transitioning. And second, they react slower compared to normal cement. The use of calcined clays represents a solution for the first problem as they are globally abundant [3]; however, after a certain substitution level, the early age properties decline.

Alternatives must be found quickly, but these alternatives need to pass specific standards to be used confidently. Since cement substitution is the most realistic way to reduce the environmental impact of concrete, a higher level of substitution could be used if the cement clinker component was more reactive. Hence, when mixed with water, the higher reactivity of the clinker can counteract the low contribution of SCMs at early ages. This research aims to look at this possibility and provide knowledge for further reduction of the environmental impact of cementitious materials.

1.2 Towards a sustainable cement: Zn as a potential solution?

Cement is composed of four main phases: tricalcium silicate (C_3S) or alite, dicalcium silicate (C_2S) or belite, tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). These phases compose clinker which is ground together with gypsum to form cement [4].

The hydration of cement is a complex process in which the different cement phases react with water to produce hydrated phases. This reaction is exothermic (releases heat) and can be followed over time by isothermal calorimetry [4]. To reduce its complexity, researchers have focused on the reaction of alite, the major phase which represents around 50-70% of the cement composition. Figure 1-1 shows the hydration curve of alite. At the beginning of the reaction, a first peak is seen, and it corresponds to the dissolution of the phases (0). This period is followed by a slowdown (I) and a dormant period of low chemical activity (II). Then, the reaction increases in the acceleration period (III), where about 50% of the alite reacts. In this period, the mix sets and develops the early strength, which increases from two to four times in 28 days [5]. Afterward, a deceleration occurs (IV), and then after about 24 hours, the reaction is slow but continues. Several theories have been proposed to explain the transition between the different stages. But these theories remain under discussion [4].

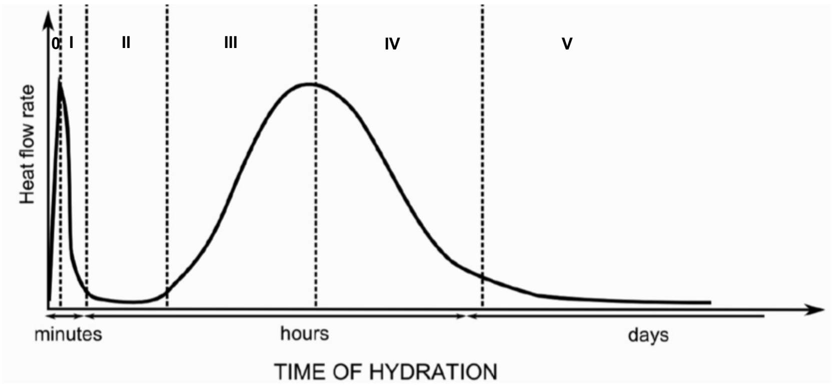

Figure 1-1: Heat of hydration of alite, the main cement phase (modified from [4]).

When SCMs substitute part of the cement, the early age properties are reduced because, as shown in figure 1-2, they react much slower compared to alite. This situation brings severe problems in construction sites, where achieving certain strength at a max of 2 days is often an essential requirement. The substitution by SCMs is then limited by their low contribution to the reaction during the first day.

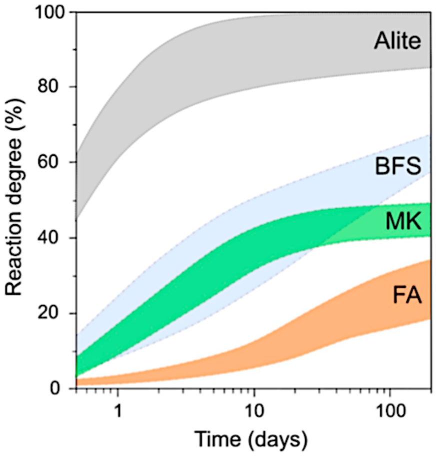

Figure 1-2: Comparison of the reaction degree of different SCMs with alite. SCMs contribution to hydration is minimal at early ages. (BFS=blast furnace slag, MK=metakaolin, and FA=fly ash) [6].

If the cement component reacted more during the main heat evolution peak, it would be possible to replace more cement and lower CO_2 emissions. The question is how to increase the reactivity?

Recent work from Bazzoni et al. [7] showed that small percentages of ZnO in the crystalline structure of C_3S (alite pure phase) significantly increase the heat released (figure 1-3) during the main heat evolution peak. They found by transmission electron microscopy (TEM) that this enhancement in hydration heat was related to a change in morphology of the main hydration product, calcium silicate hydrate C-S-H, often seen as needles. The length of these needles was increased in the presence of zinc (figure 1-3). The doping with Zn also gave some insights into the hydration mechanisms; they suggested that the growth of the C-S-H controls the acceleration period until no free surface is available. Also, with this transition to the deceleration period, there is a different growth mechanism since the formation of the inner C-S-H starts at this point. This hypothesis was supported by Ouzia et al. [8], who developed a model based on the assumption that C-S-H nucleates and grows as needles in which all the parameters were constrained by experimental data. The doping experiments fit very well with the model simulations. This supports the idea that the hydration peak can indeed be explained in terms of nucleation and growth of needles.

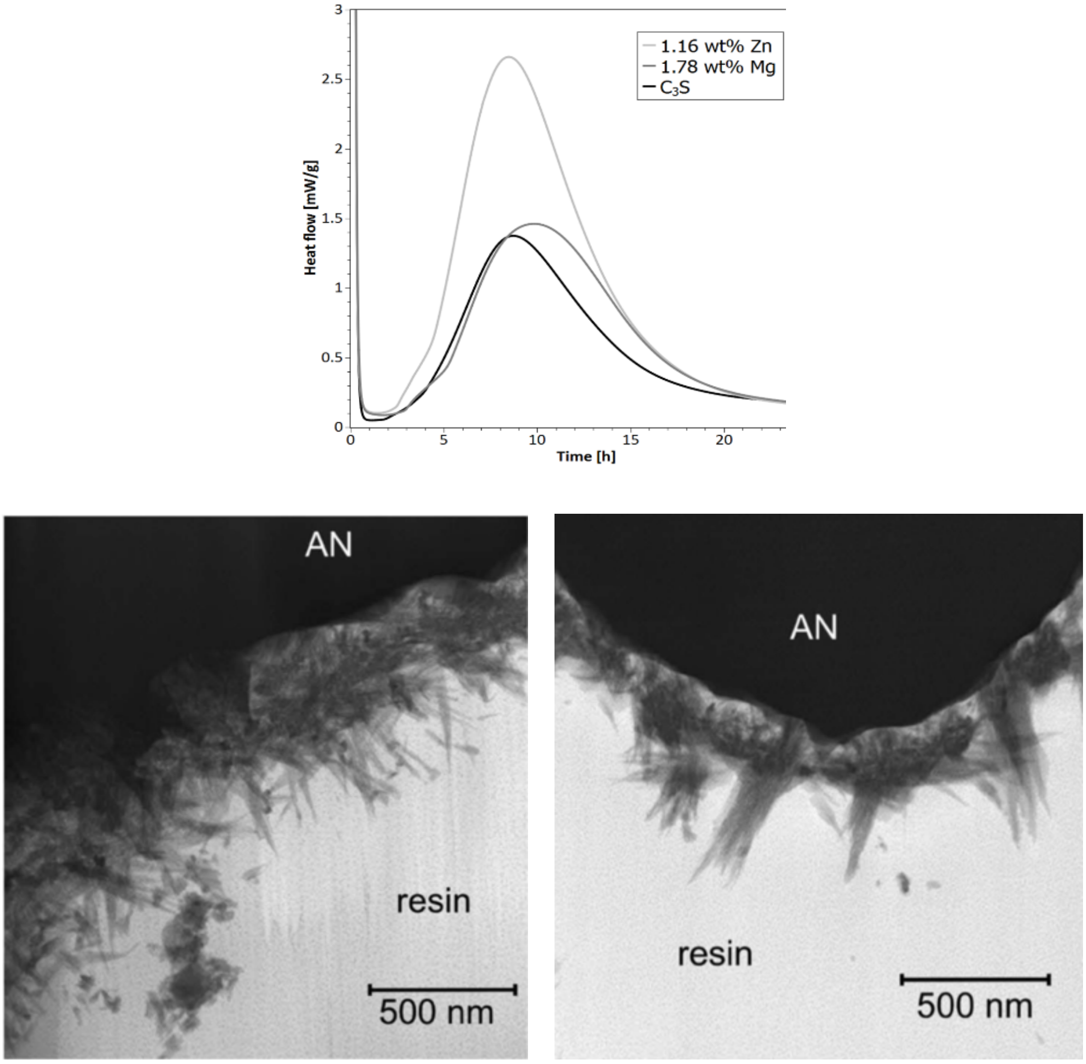

Figure 1-3: Bazzoni's doping experiment. The increase in heat is due to the growth of longer C-S-H needles [7].

The work of Li et al. demonstrated that the incorporation of zinc into C_3S has a very significant effect on early strength (Figure 1-4). The presence of 0.90% ZnO in C_3S promotes its hydration, and the compressive strength is enhanced until three days. The growth and composition of C-S-H were also affected; longer needles and clusters were formed in the presence of Zn. Also, it was found that the Zn ion is probably replacing the Si in the C-S-H structure [9].

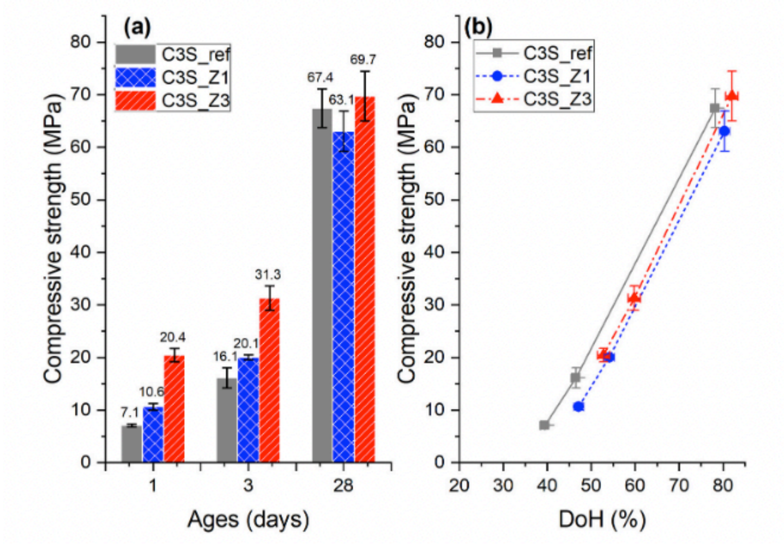

Figure 1-4: Compressive strength at early ages is enhanced with the incorporation of zinc [9].

Therefore, the effect of ZnO in C_3S shows a potential solution to increase the reactivity of the cement that is not being replaced and then counteract the low contribution of SCMs at early ages. The main challenge is to translate these effects into real cement. Even though alite represents up to 70% of the cement composition, the presence of other phases can interfere. It is known that the addition of ZnO during mixing leads to severe retardation, while the low concentration released by the C_3S hydration enhances the reactivity. This means that the ZnO must be added together with the raw materials for cement production at 1450 °C, which can also change the thermodynamics of clinker formation and Zn repartition between the phases and hence affect the hydration and reactivity.

1.3 Objectives of the research

The general objective of this work is to better understand the effect of ZnO in more realistic systems, in clinker production at a laboratory scale, and in terms of hydration kinetics. This thesis is based on the following research questions:

1. *Can the effect of ZnO seen in C_3S be translated into more realistic systems?*
2. *If not, why? And are there ways to make it work?*

The "more realistic systems" studied are alite, an impure form of C_3S with minor incorporation of other elements such as Al, Mg, and Fe, and a polyclinker system in which a grain is composed of alite and one of the aluminate phases, C_3A or C_4AF. These were synthesized with 0, 1, 3, and 5% ZnO to determine the optimal concentration and study the phase distribution and Zn repartition by scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (SEM-EDX). Additionally, the hydration–reactivity was studied by isothermal calorimetry at 20 °C. The powder characterization plays an important role, too, so the particle size and the specific surface area of the doped systems are measured by laser diffraction and N_2

adsorption with the Brunauer-Emmett-Teller method (N_2-BET), respectively. Furthermore, the phase composition of the synthesized samples is checked with X-ray diffraction (XRD).

This project is part of a bigger project called “Impact of minor elements on cement hydration.” This research is project 1, which focuses on real cementitious systems. The other two are focused on synthetic C-S-H and atomistic modeling, aiming to answer where the Zn is situated in the C-S-H structure. Together, the project intends to understand the role of minor elements, particularly Zn, on cement hydration.

1.4 Structure of the thesis

The thesis is divided into six chapters, five of which, in addition to this introductory chapter, are structured as follows:

Chapter 2: “The effect of ZnO in clinker and hydration” is a literature survey that summarizes different research done on minor elements in clinker production and their effect on the reactivity, focusing on ZnO. It also shows basic knowledge about the clinkerisation process, thermodynamics, and phase diagrams that help to better understand the effect of ZnO in more realistic systems.

The next three chapters correspond to the experimental results and are written in paper format for submission in peer-reviewed journals.

Chapter 3: “Effect of ZnO in more realistic systems” shows a comparison between alite and a polyclinker with 90% alite and 10% C_3A and the effect of different concentrations of ZnO in terms of hydration kinetics, zinc repartition, and phase distribution. It also provides a new hypothesis explaining the different effects observed and a potential solution to make it work.

Chapter 4: “Study of the retention of Zn in alite” investigates the possibilities of Zn retention by alite in more realistic systems, and three approaches are presented. One of them is related to the C_3A-polyclinker with a thermal treatment. The other two are similar studies to chapter 3, but in this case, the polyclinker is designed 90% alite and 10% C_4AF to evaluate the phase preferences of zinc. In addition, the effect of the quantity of the interstitial material on these preferences is studied in a polyclinker designed 95% alite and 5% C_4AF.

Chapter 5: “Interaction between sulfates and Zn in alite hydration” studies the impact of gypsum addition in Zn-doped alite, and a possible explanation for the retardation observed is given.

Chapter 6: “Conclusions and perspectives” is the closing chapter that summarizes the research and the findings. Perspectives and next steps are proposed.

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Chapter 2 The effect of ZnO in clinker and hydration

Contents

Minor elements in cement have been of interest to many researchers for a long time, and it has been studied with different focuses through the years leading to different conclusions. In the ’50s, minor elements were used to study the crystal structure of clinker phases and define them to determine the clinker composition. In the 70s, the focus changed to minor elements and their effects on cement hydration. However, no clear mechanisms were identified due to the lack of advanced analytical methods. Later, it was concluded that ZnO affects the crystal structure and that the reactivity of the C_3S depends on the polymorph type. Yet, no detailed investigation of hydration mechanisms was done. In the last decade, attention was changed to the effect of minor elements on cement reactivity and obtaining the limits that can enhance its hydration. ZnO, in particular, can be added in two ways: as an admixture or as raw material. From many studies, the majority, have concluded that ZnO retards cement hydration no matter the way it is added. The mechanism will be discussed in this section. Conversely, in the work of Bazzoni et al and Li, the reactivity of the alite is increased with the incorporation of Zn, and this enhancement is related to the C-S-H nucleation and growth, as mentioned previously.

As this thesis is based on the hypothesis that Zn in alite works and its main objective is to find ways to translate these effects into more realistic systems, it is essential to study the impact of ZnO in clinkering and hydration. The start point is to understand what people have done in these subjects, find the gaps, and look at solutions to improve reactivity. This chapter presents the theories related to clinker chemistry and a literature survey of the effect of minor elements, particularly ZnO, on clinkerisation, hydration, and the link between these two domains.

2.1 Clinker Chemistry

Portland cement is composed of clinker and calcium sulfate dihydrate (gypsum). At the same time, clinker is constituted of four main phases. The silicates, tricalcium silicate (C_3S) and dicalcium silicate (C_2S) called alite and belite in real systems where impurities are present. And the aluminates, tricalcium aluminate (C_3A), and calcium alumino ferrite solid solution ($C_2(A,F)$) usually referred to as C_4AF. These phases result from heating a mix of limestone and clays at around 1450 °C. This section presents a summary of the composition of Portland cement clinker and its production process, including some aspects of high-temperature clinker chemistry. In the end, a review of the effect of ZnO in clinker through the years is given.

2.1.1 The constitution of Portland cement clinker

A mix of calcium carbonates and aluminosilicates is burned together to result in a granular material called clinker. [1] The word clinker comes from Dutch *klinkaerd* or *klinken* which means “to ring” and it was so called as it does make a similar sound during the clinkering process. Portland cement clinker is composed of around 67% CaO, 22% SiO_2, 5% A_2O_3, 3% Fe_2O_3, and 3% of other components such as MgO, alkalis, or free lime. In terms of phase composition, around 50-70% alite, 15-30% belite, 5-10% aluminates, and 5-15% ferrite [1].

Tricalcium silicate, $3CaO.SiO_2$, or in cement notation C_3S, is the major phase in Portland cement as it has a decisive role in hydration kinetics and strength development. Pure C_3S is the result of the solid-to-solid reaction between C_2S and CaO above 1250 °C. It exists in different polymorphs, three triclinic, three monoclinic, and rhombohedral (figure 2-1). Then, pure C_3S has a triclinic T_1 structure at room temperature.

$$T_1 \xleftrightarrow{620\ °C} T_2 \xleftrightarrow{920\ °C} T_3 \xleftrightarrow{980\ °C} M_1 \xleftrightarrow{990\ °C} M_2 \xleftrightarrow{1060\ °C} M_3 \xleftrightarrow{1070\ °C} R$$

Figure 2-1: The polymorphs of pure C_3S (T = triclinic, M = monoclinic, R = rhombohedral) (modified from [1]).

The term *alite* is used in real systems since C_3S can incorporate minor amounts of impurities such as Al^{3+}, Mg^{2+}, and Fe^{3+} among others, in its crystalline structure. [1][2][3] These impurities can stabilize the different high-temperature polymorphs to room temperature. For example, in real clinkers, the presence of MgO and sulfate impurities can stabilize the M_1 and M_3 polymorphs respectively [4]. No clear evidence has been provided to demonstrate that the different polymorphs affect the reactivity of alite [3]. X-ray diffraction can be used to identify the polymorph, or a mixture of polymorphs as seen in figure 2-2 However, this identification in clinkers is complicated as other peaks can overlap especially between 32° - 33° 2θ (Cu Kα radiation) [1].

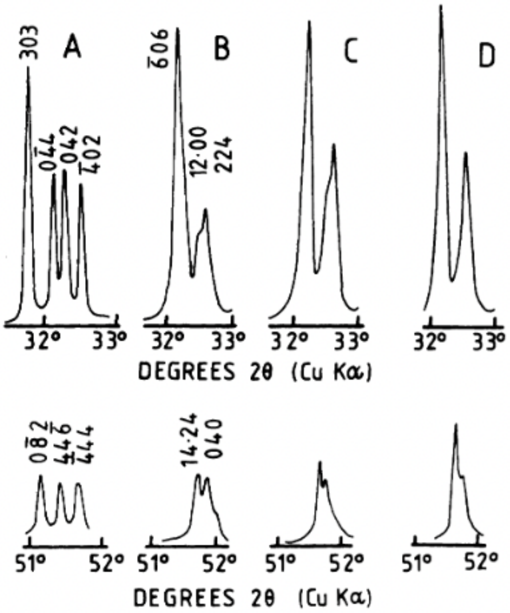

Figure 2-2: Angular windows of XRD patterns of A= T_1 in C_3S; and alite in clinkers B = M_3, C = M_1+M_3, and D = M_1 [1].

Dicalcium silicate, $2CaO.SiO_2$ or C_2S is the second-most abundant phase in Portland cement clinker. Similar to alite, it can incorporate minor elements in its crystalline structure and then is called *belite* [1]. It reacts with water like alite but much more slowly, so its contribution to the strength is at a later age. It also has different polymorphs (figure 2-3), only the inert (γ-C_2S) is stable at room temperature. The main phase in clinkers is β-C_2S , which must be stabilized by rapid cooling or with minor elements. The transformation from β-C_2S to γ-C_2S causes a phenomenon called "dusting", since γ-C_2S crystals are less dense than β-C_2S [1][3][5].

$$\begin{tikzcd}
\alpha \arrow[r, shift left, "1425°C"] & \alpha'_H \arrow[l, shift left] \arrow[r, shift left, "1160°C"] & \alpha'_L \arrow[l, shift left] \arrow[r, shift left, "630\text{–}680°C"] & \beta \arrow[l, shift left, "690°C"] \arrow[r, "<500°C"] & \gamma \arrow[lll, bend left, "780\text{–}860°C"]
\end{tikzcd}$$

Figure 2-3: The polymorphs of pure C_2S (H = high and L = low symmetry) [1].

The phase diagram of the CaO – SiO_2 system is shown in figure 2-4 where the different C_2S polymorphs are seen. Below 1250 °C the C_3S may decompose into C_2S and CaO in equilibrium conditions [1]. The effect of cooling will be discussed in the next section.

On the other hand, the pure tricalcium aluminate, $3CaO.Al_2O_3$ or C_3A, does not exhibit polymorphism [1]. It is cubic but its structure can be modified with Ca^{2+} substitution by minor elements substitution such as Na^+, $Mg^{2+,}$ and K^+. Al can also be substituted by Fe^{3+} and Si^{4+}. In clinkers, the cubic and the orthorhombic structures are the most common, alone or together. The cubic form is often found mixed with dendritic crystals of ferrite, and the orthorhombic is observed as a dark interstitial material. Moreover, the content of impurities is higher for the orthorhombic than for the cubic form.

The cooling rate has an impact in the incorporation of minor elements as it was found that slow cooling decreased the substitution of Ca^{2+} by Mg^{2+}. The C_3A phase is highly reactive and is controlled by the addition of calcium sulfate during grinding. It has been found that the substitution of alkali metal ions retards its hydration, and this effect is more pronounced in cubic than orthorhombic structures [1][5].

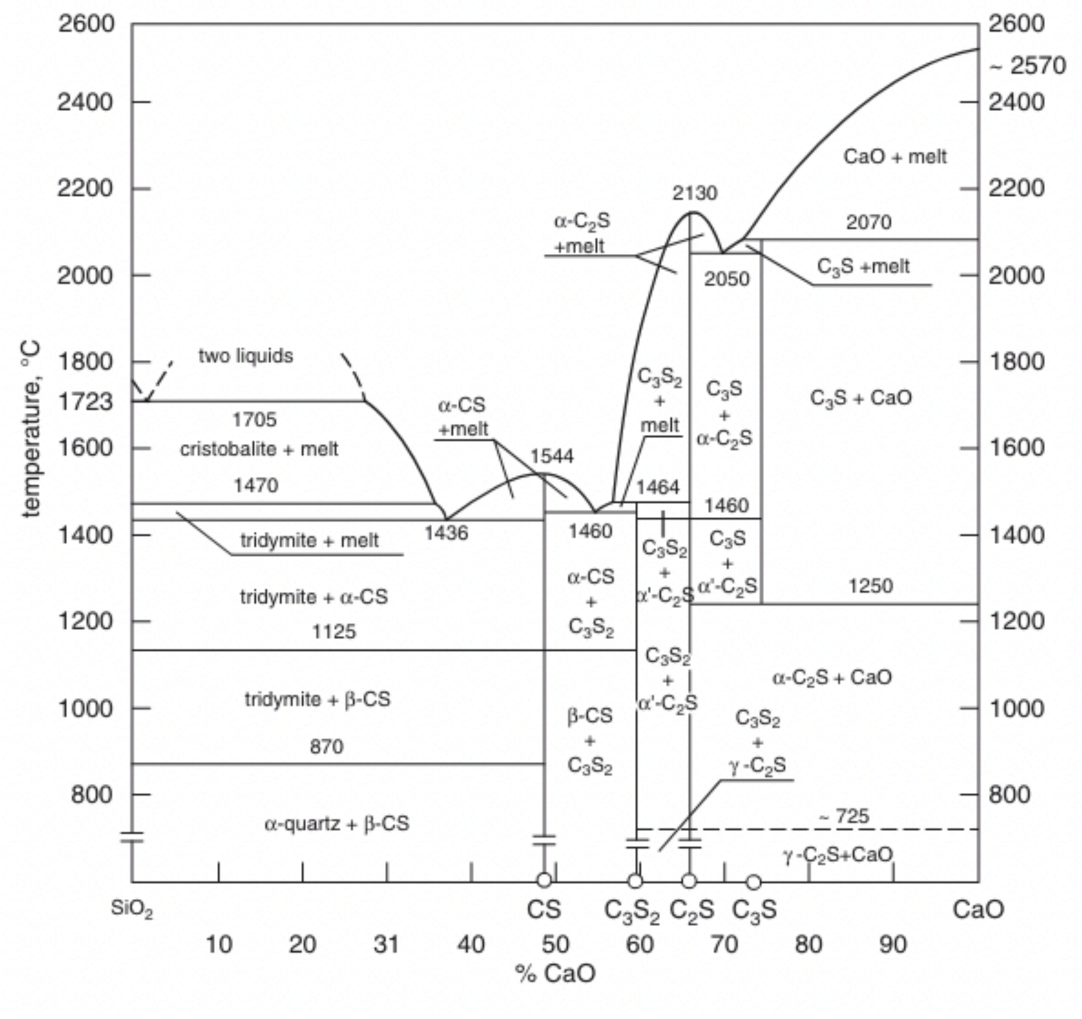

Figure 2-4: CaO – SiO_2 system [5].

Finally, the ferrite phase, $2CaO.(Al_2O_3,Fe_2O_3)$ or C_4AF, also known as brownmillerite and has an orthorhombic structure [1]. In clinker, however, its composition is different since it contains around 10% of substitution by other elements and less Fe_2O_3. Mg^{2+}, $Si^{4+,}$ and Ti^{4+} commonly replace Fe^{3+}, and the A/F ratio

(Al_2O_3/Fe_2O_3) depends on the burning conditions. When ferrite is close to its ideal composition, it has a yellowish-brown color, but in clinkers, it is almost black [1]. This is associated with the presence of more Mg^{2+} or Zn^{2+}. These substitution ions cause oxygen vacancies probably filled during cooling and then oxidation of the Fe^{3+} to Fe^{4+}. The cooling rate has also a role in this phase, quenched samples contain poorly crystalline ferrite affecting its identification by XRD [1][5].

Figure 2-5 shows one of the most important diagrams in cement chemistry [1][3]. It is the equilibrium diagram of the $CaO – Al_2O_3 – SiO_2$ system, the three most important oxides components. Even though this strictly speaking only represents white clinkers (with no iron), it is useful to predict what phases will form from certain compositions. The region of Portland cement clinker is marked with a green circle. As seen, different phases can form depending on the dosage of the different components. Therefore, a good homogeneity of the raw materials is necessary to avoid the formation of other phases promoted by locally different chemical compositions [1][6].

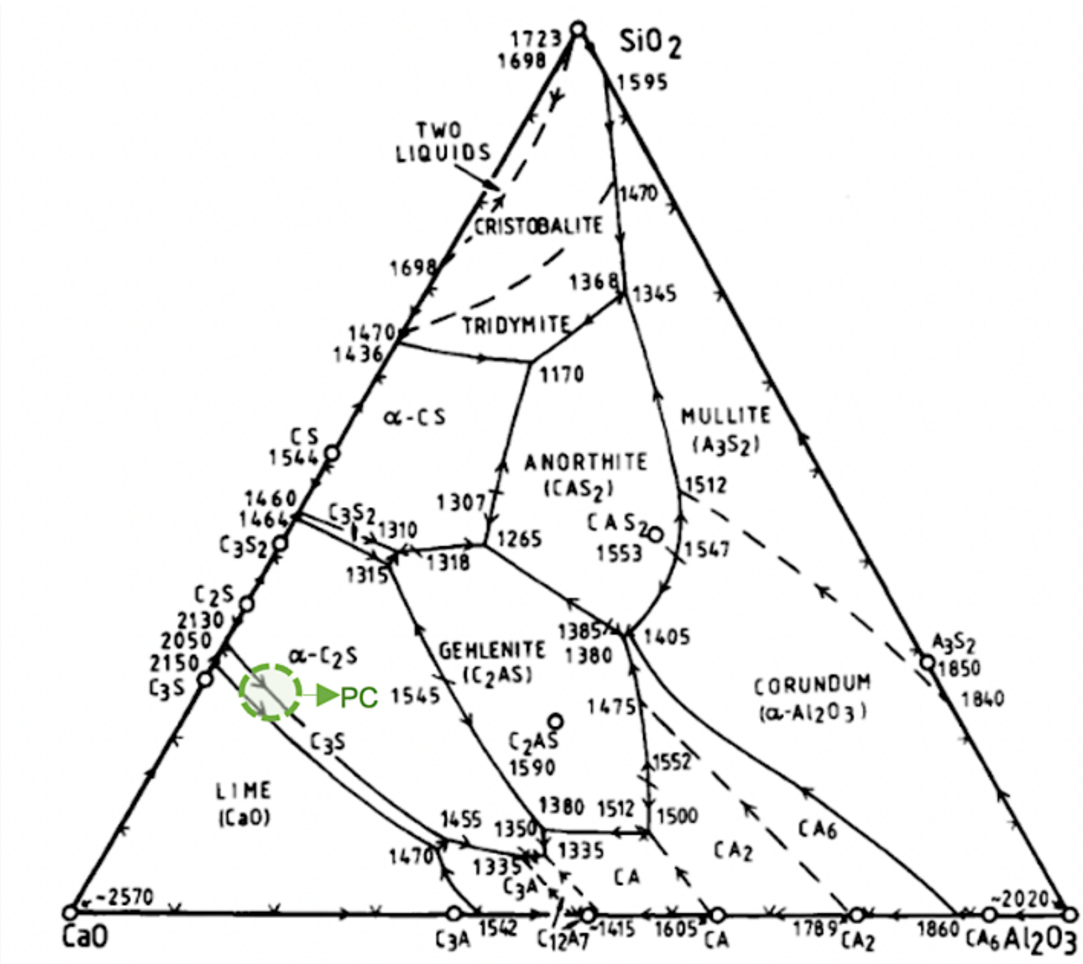

Figure 2-5: Ternary diagram of the system $CaO – Al_2O_3 – SiO_2$. The green area corresponds to the composition of Portland cement clinker. Modified from [1].

The region of interest for Portland cement clinker is shown in figure 2-6. It helps to foresee how the melt with given composition will crystallize. For example, in a melt of composition P, C_3S will crystallize first, then it will reach the boundary between the C_3S and C_2S primary phase fields. C_2S starts to crystallize as well, and the liquid composition moves on that boundary until the isotherm at 1500 °C is reached. So, basically, the phases in equilibrium at 1500 °C will be C_3S, C_2S and a liquid with composition X. If the same analysis is done for the point S that lies below the line C_3S-Z, the phase assemblage will contain CaO. Furthermore, considering industrial clinkering conditions, the line from C_3S to the invariant point at 1470 °C where C_3S, C_3A, CaO, and a melt coexist, is a good indication for CaO limits, as it is desirable to maximize the content of C_3S and minimize the one of CaO [1][5].

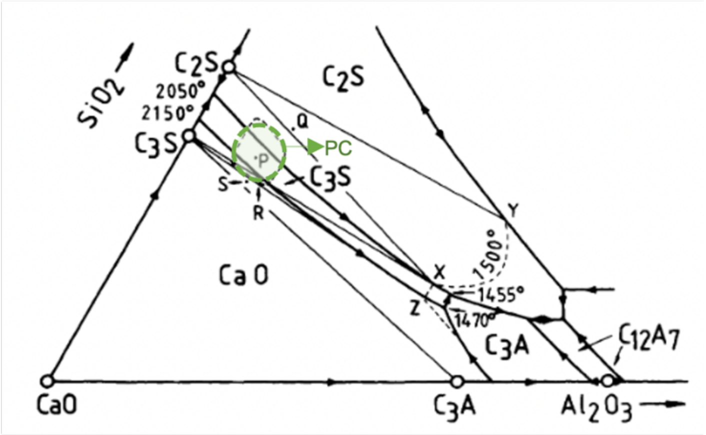

Figure 2-6: Portland cement clinker region of interest of the ternary diagram of the system CaO – Al_2O_3 – SiO_2 [1].

The system CaO – Al_2O_3 – SiO_2 – Fe_2O_3 is a better representation of normal Portland cement clinker as it is composed 95% of these oxides [1][3]. The phase relations of interest for Portland cement clinker are shown in figure 2-7. These types of diagrams are more complicated to read because the boundary lines between the primary phase fields found in ternary diagrams become surfaces in quarternary systems between primary phase volumes. Also, the invariant points become lines. The quarternary system can be seen as a combination of four ternary diagrams: CaO – $C_{12}A_7$ – C_2S, CaO – C_2S – C_4AF, CaO – $C_{12}A_7$ – C_4AF, and C_2S – C_4AF – $C_{12}A_7$ [1][3][5].

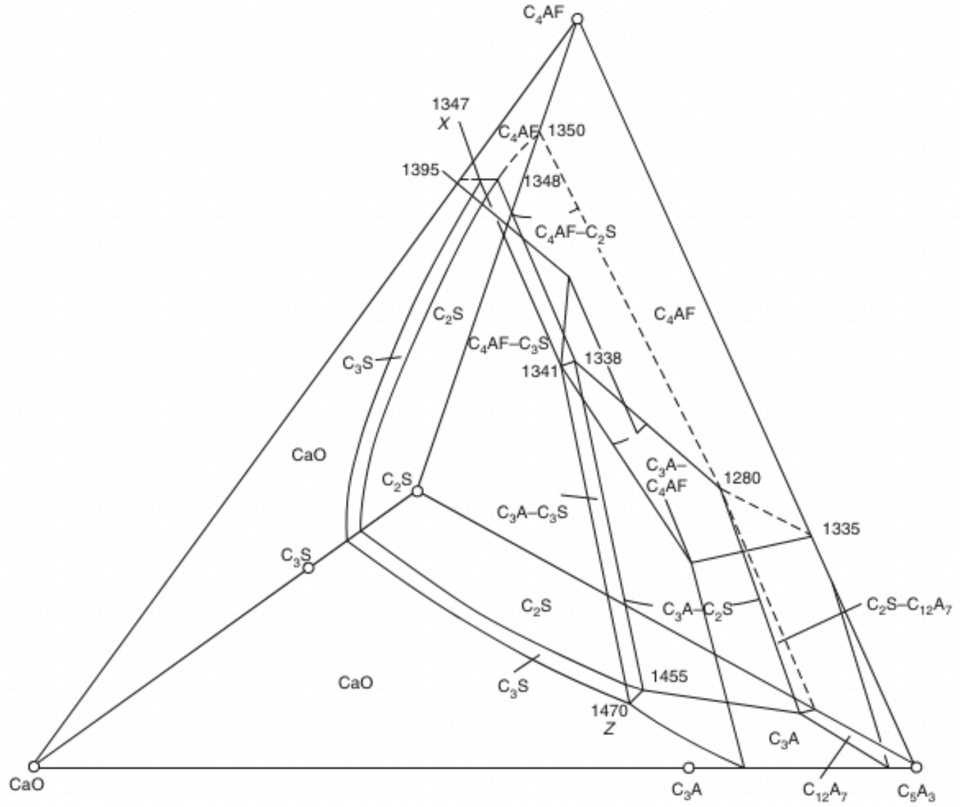

Figure 2-7: The pseudo system CaO – Al_2O_3 – SiO_2 [5].

There are different invariant points but two of them, at 1341 °C and 1338 °C, involve the phase composition of Portland cement clinker [1][3]. In the first one, CaO, C_3S, C_3A, and C_4AF coexist in equilibrium with the liquid phase. In the second invariant point, the phases in equilibrium with the melt are C_3S, C_2S, C_3A, and C_4AF. Any raw material composition inside this phase volume (tetrahedron C_3S-C_2S-C_3A-C_4AF) will result in a clinker with these four phases. A composition on the right of this volume will result in a combination of C_2S, C_3A, C_4AF, and $C_{12}A_7$, and on the left will result in C_2S, C_3A, C_4AF, and free CaO. Both scenarios are to be avoided in clinker production as no C_3S is formed and free CaO causes destructive expansion (and from the sustainability point of view is a waste of energy and raw materials) [1][5][6].

Therefore, as suggested previously in [5][6], this phase diagram helps to predict what phases will be present in the final clinker in equilibrium conditions. However, in real clinker production, the raw material, process conditions, and/or minor elements will also affect the clinker phase composition. For example, if a composition in the tetrahedron C_3S-C_2S-C_3A-C_4AF on the left side near the C_3S primary phase field, close to the primary phase field of CaO, is fast-cooled, the product will contain free CaO [6]. Nevertheless, the cooling process is always fast in industrial conditions, so the clinker will always contain a little amount of CaO, and this is why the line C_3S – Z in figure 2-6 is useful to set the maximum amount of free CaO [5].

2.1.2 The chemistry of the clinkering process

In the production of Portland cement clinker, a fixed mix design of raw materials, commonly limestone and clay, are mixed and burned at 1450 °C in a rotary kiln inclined with a slope of 3-4% from the horizontal [1]. The pre-treated raw materials enter from one end and go through the kiln, which rotates for better homogenization, and then reach the end point where a flame is located. This zone is called “burning zone” or “sintering zone” and is where nodules of clinker are formed and then cooled down. The cooling process starts inside the kiln, in between the flame and the exit, and then the nodules leave the kiln and enter the cooler system [1].

Different reactions take place in this process as seen in the diagram of figure 2-8. Below 1300 °C the calcite decomposes as well as clay minerals, and calcite or lime reacts with quartz, and the products from the clay minerals decomposition to form belite lime, aluminate, and ferrite [1]. These reactions are solid to solid, and if the homogeneity is ensured, there is no liquid formation below 1338 °C (see phase diagram in figure 2-7). The diffusion of Ca^{2+} into the SiO_2 particles forms belite. The aluminate is formed with an intermediate phase $C_{12}A_7$ through the diffusion of Ca^{2+} into Al_2O_3 particles. The ferrite phase appears after the Fe^{3+} ions diffuse into the aluminate phase replacing Al^{3+}. Inhomogeneities always exist, and liquid might form in local areas helping the reactions to occur. Moreover, the aluminate and ferrite formed might not be the same as in the final clinker [1][3][6].

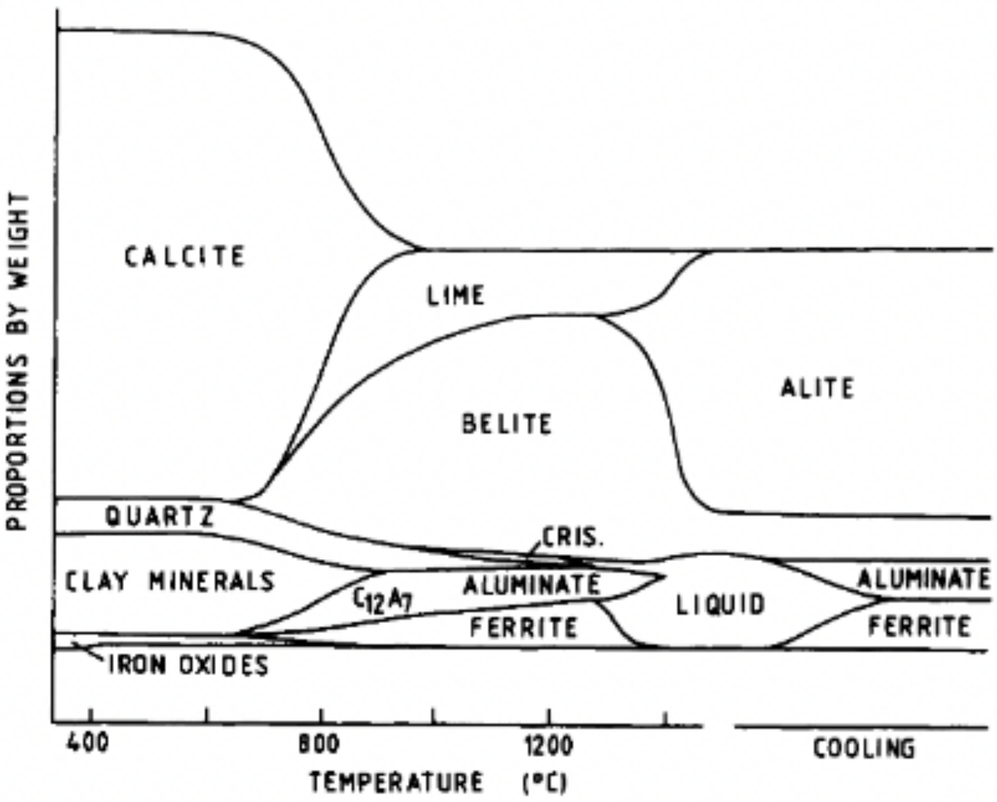

Figure 2-8: Raw representation of the reactions during Portland cement clinker manufacture. The composition varies with the raw materials used [1].

Between 1300 – 1450 °C, known as clinkering zone, the aluminate and ferrite melt, which leads to nodulization of the solid particles where they stick together [1]. The system is then composed of 20 – 30% liquid that promotes the reaction among belite and lime to form alite. Therefore, alite is formed through solid to liquid, liquid to liquid reactions, or both, in where Ca^{2+} ions, from the dissolution of lime in the melt, diffuse into belite. As this diffusion is favored with the temperature, at high clinkering temperatures high supersaturation is reached, more nuclei can be formed, and then alite has a smaller crystal size. At low clinkering temperatures, the melt has low supersaturation, so fewer nuclei are formed. Nevertheless, alite crystals can grow in the burning zone [1][4].

Finally, the clinker is rapidly cooled down below 1250 °C to avoid the decomposition of alite into belite and free lime (see phase diagram in figure 2-4). During cooling, the aluminate and the ferrite phase recrystallize from the melt, and the clinker is obtained. The A/F ratio plays an important role in the final composition of the clinker [1]. A ratio lower than 1.38 is an indication that more crystalline C_4AF will form. On the contrary, with a higher A/F ratio in the raw materials, more C_3A is expected to crystallize [1][3][6].

As seen, the clinkering process is highly dependent on the presence of the liquid and the temperature at which this phase forms. The inhomogeneities of the process and composition of the raw meal can shift the temperature toward lower values. In the system C_3S – C_2S – C_3A the eutectic temperature is 1455 °C (figure 2-5). However, when Fe_2O_3 is in the raw materials, this temperature drops to 1338 °C, and it goes even lower to 1280 °C when Na_2O and MgO are added [1]. The clinkering range is also affected by the quantity of liquid phase formed. This range represents the maximum and minimum liquid content to produce clinker with acceptable quality. The quantity of the liquid can be altered with fluxes, agents that increase the amount of liquid phase at a certain temperature and then promote the reactions. The most common are Al_2O_3 and Fe_2O_3 which help the formation of alite. Another type of agents are mineralizers; they change the equilibria and promote the formation of a particular phase by incorporation in one or more solid phases. Calcium fluoride (CF_2) is known to act as a mineralizer and also as a flux agent promoting the formation of alite [1][3].

Moreover, the viscosity and surface tension of the melt are important to consider. Low viscosity values accelerate the dissolution of lime and belite, and enhance the diffusion of ions through the liquid, so alite is formed faster. Lower surface tension values promote the wetting of the particles and allow better penetration into the pores [1][3]. Foreign elements in the clinker raw meal can affect the viscosity and the surface tension of the melt. Figure 2-9 shows a viscosity decrease with heavy metals such as Fe, Ti, and Zn, among others [5].

The rate at which the clinker is cooled down affects the conditions of crystallization and hence the clinker composition and quality [1] [7]. With a slow cooling, large crystals of aluminate and ferrite phase are produced. Conversely, with fast cooling, a mixed microstructure is favored, in where the ferrite forms dendrites in an aluminate matrix. Additionally, the cooling rate seems to affect the degree of crystallinity of these two phases. In industrial situations, the cooling is fast and might lead to a melt solidification as glass combined with the crystallized phases [3]. However, in practice, this is not closely controlled.

In clinkers with MgO, the cooling conditions change its distribution [1]. A rapid cooling traps MgO in the aluminate and ferrite phases, and a low amount of small periclase crystals are formed. With a slow cooling, a minor amount is retained in the interstitial phases, and the rest forms large periclase crystals (with a potential risk of expansion).

The cooling rate also affects the colour of the clinker [3]. Slow cooling results in a dark-brown clinker while a quenched sample tend to be brownish yellow, related to the presence of glass. The presence of MgO darkens the clinker if it is slow cooled and Mn gives a brown color.

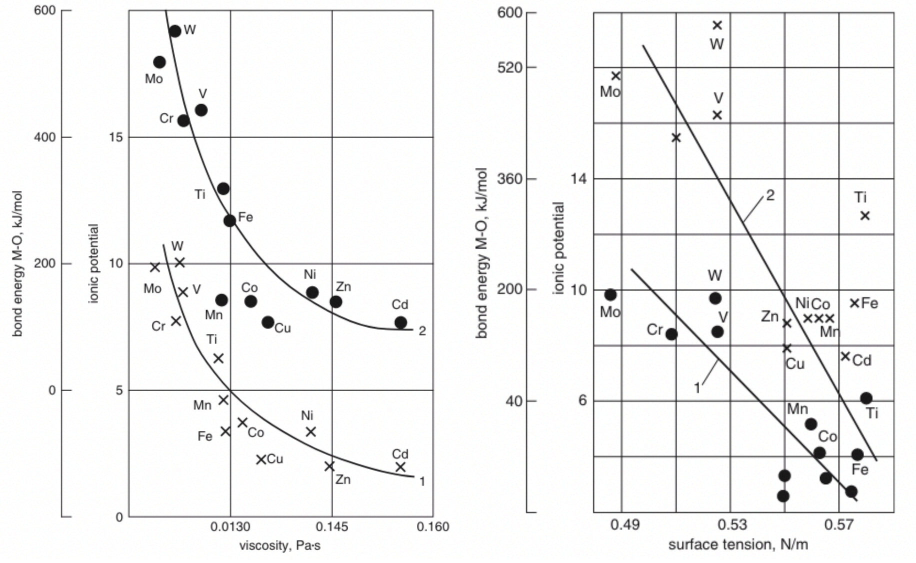

Figure 2-9: Viscosity and surface tension of the liquid phase is decreased by foreign elements [5].

2.1.3 Effect of minor elements, particularly ZnO

Minor elements from the raw materials, fuel, the kiln, or added intentionally (as fluxes or mineralizers) affect the clinkerisation process as well as the hydration properties. These effects can be positive or negative depending on the element and its concentration. It is known that K_2O and Na_2O decrease the temperature at which the liquid is formed, increase its viscosity, and alter the crystalline structure of C_3A to orthorhombic. The presence of SO_3 also decreases the melting temperature plus the viscosity of the melt. Titanium and zinc decrease the viscosity of the melt; however, their effects on clinkering and subsequent properties are not fully understood [1]**.**

The effect of Zn in clinker is not a new study, it has been investigated throughout the last century and many different conclusions often contradictory, have been drawn. In 1980 Odler and Schmidt [8] synthesized clinker with ZnO addition by the pellet method fired at 1450 °C for 1 hour and cooled in air. They proposed that ZnO can be used as a mineralizer as the amount of free lime decreases with the ZnO dosage. This effect was also observed with the decrease in the firing temperature. It led them to suggest that ZnO accelerates phase formation by decreasing the temperature at which the liquid phase appears. Even when the study was focused on ZnO as Zn source, they found that similar effects were observed with other Zn compounds such as ZnS, $ZnSO_4$, or $Zn_3(PO_4)_2$. However, little evidence was presented. The phase compositions were obtained by means of optical microscopy and showed an increase in the alite, and in the interstitial content as ZnO dosage increased, whereas the C_3A decreased. This was related to the amount of free lime; more lime is available for alite formation as part of the calcium ions are replaced by Zn ions. Also, with the presence of $C_2(A, F)$, less lime reacted with the alumina, and hence there is more available to react with the silica. In their clinkers, Zn was found to be concentrated close to the interface of the interstitial material. The concentration in alite was not significant, but neither was not zero. Even so, only one picture is seen with a line scan spectrum [8]. To give that conclusion, it is necessary to study the repeatability of these results, but this does not appear to have been done. In terms of hydration properties, the non-evaporable water experiments showed an alite retardation with 3% ZnO for up to 28 days. They also concluded that the C_3A seems to be more reactive due to ZnO doping as the gypsum was consumed faster and the ettringite formed rapidly; however, they do not show either these results or mention how they measured it. Finally, the compressive strength at 28 days was significantly increased with lower than 1% ZnO additions, but again no explanation was given.

Three years later, Odler and Abdul-Maula [9] did similar research, but this time focused on the effect of ZnO doping on C_3S hydration. The synthesis process was changed compared to the previous study. In this case, the doped C_3S was obtained by mixing calcium oxalate, silica gel, and ZnO; the burning temperature was 1500 °C, and the samples were taken out every two hours and reground. However, no sintering time was reported neither was the pellets size. They concluded that up to 4.7% ZnO can be incorporated into the C_3S crystalline structure, and the increase of dosage changes the polymorph of this phase as well as the temperature at which C_3S is formed. Their hydration studies showed an increase in the heat released with ZnO dosage and this enhancement was related to the different polymorphs being the rombohedric the most reactive.

A decrease in the clinkerisation temperature with ZnO was also observed by Kakali and Parissakis [10]. They studied the effect of ZnO in real clinkers by mixing the industrial raw material of Portland cement with different amounts of ZnO. The samples were fired up to 1450 °C in an electrical furnace and cooled down in the air. They concluded that ZnO lowers the clinkerisation temperature, 50 °C with 1.5% ZnO and 100 to 150 °C with 2-4% ZnO. Besides, it promotes solid-to-solid reactions and the combination between CaO and

Al_2O_3. Moreover, they studied the crystallization of the melt in the presence of Zn and found that the melt temperature lowers as more Zn is added. This was related to the formation of a eutectic melt and a higher amount of liquid. Also, they found the formation of a new phase, $2CaO.ZnO.SiO_2$, when more than 1.5% ZnO is added and changes the color of the clinker to brown.

On the contrary, Bolio-Arcéo and Glasser [11] proposed the formation of a new phase with aluminum $Ca_6Zn_3Al_4O_{15}$ ($C_6Z_3A_2$) instead of a calcium zinc silicate, when more than 1 wt% ZnO is added to the raw materials. They studied the systems C-Z-A and C-Z-F by mixing pure grade oxides and burned at the subsolidus temperatures. In their findings, two new phases C_3ZA_2 and $C_6Z_3A_2$ were reported. Moreover, they confirmed that $C_6Z_3A_2$ can coexist with the other clinker phases, and it is a product of the liquid phase crystallization during cooling; the amount is enhanced by the incorporation of Mg. Additionally, $C_6Z_3A_2$ mixed with gypsum, calcium hydroxide, and water forms an ettringite-like phase that could explain why ettringite was formed promptly in the Zn doped clinker even when less C_3A was formed as shown in Odler and Schmidt research.

C_3ZA_2 was also observed by García-Díaz et al. [12] with 2% ZnO in the raw materials. However, they concluded that ZnO did not show a mineralizer effect, and it works only as a flux, in contrast with the study of Kakali and Parissakis. Also, they did not identify a Zn silicate phase, but they did identify C_3ZA_2 in clinkers doped with 2% ZnO.

Stephan et. al [13]studied the influence of Zn and other minor elements on the properties of clinker phases separately. The C_3S doped with 2.5 wt% of Zn (~3 wt% ZnO) showed a longer induction period compared with the reference. This result diverges from that of Odler and Abdul-Maula, in which Zn increases the heat released by C_3S without retardation. However, the retardation was explained by the possible formation of calcium zincate $Ca(Zn(OH)_3)_2)*2H_2O$ once the sample is mixed with water. More about this retardation mechanism will be discussed in the next section. Despite this negative effect, the alite peak was higher for the doped sample. However, no explanation was given. They also look at the hydration products under the SEM to identify where the minor elements were concentrated. For Zn samples, less "extensive areas" of portlandite and C-S-H were found. But, again, no SEM images were shown.

The same authors also worked with C_3A and C_4AF [14]. Doping C_3A with more than 5 wt% Zn did not change the crystal structure, and free ZnO was found, as well as in C_4AF. A low concentration of Zn, less than 0.5 wt% Zn, seemed to not affect the hydration of C_3A. Is a higher amount of Zn that causes slight retardation and in the calorimetry curve, a second peak is observed. The retardation was justified by the presence of $Ca(Zn(OH)_3)_2)*2H_2O$ detected by XRD. No explanation was provided for the appearance of this second peak. Regarding C_4AF hydration, Zn showed slight retardation and an increase in the heat released. With SEM they concluded that 2.5 wt% Zn affects the morphology of the C_3AH_6, promoting more defects. However, it is not possible to see this in the pictures given. What is seen, besides the C_3AH_6, is a needle-like and an amorphous phase that they analyzed with EDS and contains a high concentration of Zn. The needle-like phase showed concentrations of Ca too, and they concluded that it most probably is $Ca(Zn(OH)_3)_2)*2H_2O$.

Barbarulo et. al [15] studied the influence of MgO on the negative effect of ZnO in cement hydration. Synthetic clinker doped with 1% ZnO without MgO showed retardation attributed to "white spots" observed in the microstructure. The composition of these "white spots" contains high concentrations of ZnO. Therefore, the retardation can be attributed to the fast release of Zn ions from these regions. At higher content of ZnO in raw materials, $C_6Z_3A_2$ was observed besides the "white spots". They showed that the presence of 2% MgO can somehow trap Zn as a solid solution and then the retardation is not as severe as when MgO is not present. In this sense, the Zn ions are released slower, and the delay is reduced. However, there is no proof that a solid solution MgO-ZnO is formed in clinkers, so they have this as future work.

In line with Bolio- Arcéo and Glasser, Gineys et al. [16] studied the threshold limit of different elements, including Zn, in a clinker synthesized in the laboratory. A concentration higher than 0.7 wt% of Zn shows a decrease in the C_3A content while $C_6Z_3A_2$ forms. Moreover, in clinkers with more than 2 wt% of Zn, the C_3A was not detected and only $C_6Z_3A_2$ was formed. It is interesting to see the hydration study, where they state that neither Zn nor the other elements influence cement hydration while the calorimetry curve shows a slight increase in the heat released in the Zn-clinker sample. This result disagrees with Stephan et al. where Zn retards the hydration. This difference can potentially be explained in terms of clinker synthesis. In Gineys et al. study, they synthesized the clinker with pellets method and burned at 1450 °C similarly to the work of Stephan et al. The difference lies in the cooling method. A slow cooling inside the furnace was done by Gineys et al. to allow the growth of calcium aluminate crystals. This may affect the element distribution in the clinker phases and alter the hydration properties as well. Nevertheless, the positive effect of Zn was not explained.

In recent works, Soga et al. [17] observed an increase in the C_4AF content and a decrease in the C_3A, with no changes in the silicate phases when clinkers are doped with ZnO. In this study, clinkers were synthesized by pellets method and burned at 1500 °C for 4 hours with a pre-burning at 1000 °C before. They concluded that ZnO changes the C_3A crystalline structure from cubic to orthorhombic. Besides, in accordance with Barbarulo et al. “white spots” of free ZnO were detected in the microstructure. However, in their EDS results, Zn was found to be mainly concentrated in the C_3A phase. The heat released and compressive strength was enhanced up to 0.97% ZnO, but no explanation was given. More ZnO causes a severe retardation consequence of the free ZnO.

Zhang et al. [18] worked with high ferrite clinkers doped with ZnO. The results showed an increase in reactivity with 1.5 wt% ZnO in these clinkers. They also evaluated the C_3S and the C_4AF systems separately. ZnO in C_3S retarded the hydration while in C_4AF the reactivity was improved. Therefore, they concluded that the positive effect of ZnO in high ferrite clinkers is a consequence of a Fe transformation in the C_4AF from FeO_4 to FeO_6. Additionally, they found a new phase located in the C_4AF and in the boundaries of C_3S, whose composition was estimated from the EDS analysis and resulted in $Ca_2AlZn_3O_8$.

The color is also affected by ZnO [19]. The conclusion of Li et al. in their work was that Zn increases the whiteness of white Portland cement because it also increases the content of an amorphous phase called ACn (which includes an amorphous and unquantifiable crystalline phase of C_3A and C_4AF). Therefore, it captures Fe atoms and decreases the amount of C_4AF resulting in a whiter clinker. They also observed a prolonged induction period with ZnO dosage, but higher heat released.

Doping clinker with ZnO also affects grindability. Tsivilis and Kakali [20] found a harder to grind clinker with 2 wt% ZnO and this was related to an increase in the melt content. Minor elements in the liquid phase at high temperatures change its structure, and properties and therefore affect the clinkerisation process, as well as the grindability. Similarly, In Shimosaka et al. [21] research free ZnO was found with a ZnO dosage of 1.1% or more. Additionally, they concluded that the burnability increased, and the grindability decreased with ZnO. The last is a consequence of the increase in the liquid phase with ZnO. Retardation was also observed in this study with more than 1.1% ZnO. They attributed this to the free ZnO that was not combined in the clinker phases.

As previously seen, Zn appears to have different effects depending on the systems under study, if it is a single clinker phase, lab-made clinker, or real clinker. ZnO doping in C_3S has a positive effect on hydration, and it was mainly related to the polymorphism of C_3S. In lab-made clinkers and real clinkers, Zn decreases the content of C_3A while increasing the C_4AF and retards the hydration. Besides, there are some discrepancies if Zn acts as a mineralizer or just a flux in the clinkerisation process. Furthermore, ZnO decreases the grindability of the clinkers, and this was related to an increase in the liquid phase content that crystallizes to the interstitial material upon cooling. Most of the studies agree that Zn is mainly concentrated in this phase, changes its properties and hence the hydration kinetics afterward. An important aspect is the free ZnO that remains uncombined in the clinker minerals and causes severe retardation. Thus, it is necessary to keep this value low to avoid a negative effect on hydration. Nevertheless, it is challenging to know the quantitative limits of ZnO in the clinker. In fact, this value varies depending on the author as it depends on many factors such as the raw materials used, clinker composition, synthesis process, and Zn source. The retardation mechanism of ZnO in cement hydration is discussed in the following section.

2.2 Effect on hydration: enhancing or retarding?

2.2.1 Cement Hydration

The hydration of cement is a complex process where the clinker phases react with water and gypsum (calcium sulfate) to form different hydrates. The hydration of the silicates form calcium hydroxide (portlandite or CH) and calcium silicate hydrate (C-S-H), which is the most important hydrate, mainly responsible for the mechanical properties of concrete. The C-S-H has a variable stochiometry, that is why dashes are used.

The hydration process is exothermic and can be studied by isothermal calorimetry and is often described in 5 stages. Figure 2-10 shows a typical calorimetric curve for PC, in which 4 different peaks are seen. These peaks correspond to the formation of the different hydration products. At the very beginning of the reaction, a first peak is seen, and it corresponds to the dissolution of the phases (0) and the reaction between C_3A and gypsum to form ettringite. This period is followed by a slowdown (I) and a dormant period of low chemical activity (II). Then, the acceleration period (III) is seen. This is the main hydration peak, and it is related to the reaction of the silicates to form CH and C-S-H. Afterward, a deceleration occurs (IV) during which the third peak is observed. This peak corresponds to the second formation of ettringite. Finally, there is a period of low activity and sometimes a fourth peak may be observed, corresponding with the formation of monosulfoaluminates (AFm), a product of the reaction between C_3A and ettringite when there is no more free sulfate in the system.

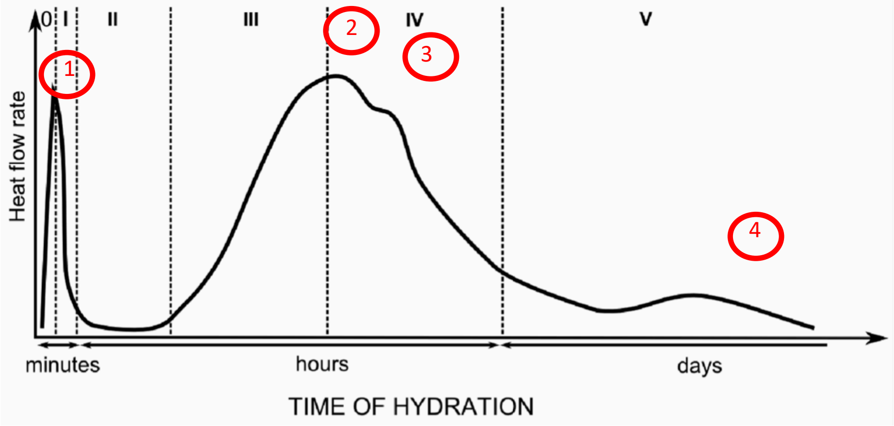

Figure 2-10: Calorimetric curve of a typical ordinary Portland Cement and its different reaction stages [22].

The C_3S in ordinary Portland cement is not pure [1]. It has minor amounts of aluminum, magnesium and iron and it is called alite. It is the main component of cement, representing up to 70% of its composition. For this reason, there is a lot of effort in understanding its reaction as a simplified cement system in a way to minimize complexity. Figure 2-11 shows the calorimetric curve of alite hydration. The difference from the previous figure is the absence of peaks 3 and 4 since no C_3A is present. The figure also shows that during the induction period (II) the amount of Ca^{2+} ions keeps increasing above the saturation level of portlandite until it reaches a maximum from where the hydrates start to precipitate. Then, the concentration decreases to the saturation level during the acceleration period. Therefore the hydrates growth controls the kinetics of this stage.

Several theories have been built to explain the transition between the different stages. However, these theories remain under discussion. A recent paper by Scrivener et al. [23] reviews these theories and most evidence suggests that the reaction up to the end of the induction period (I & II) is determined by the dissolution of the alite, which is controlled by the undersaturation of the solution during the main heat evolution peak (III & IV) the reaction is controlled by the growth of C-S-H.

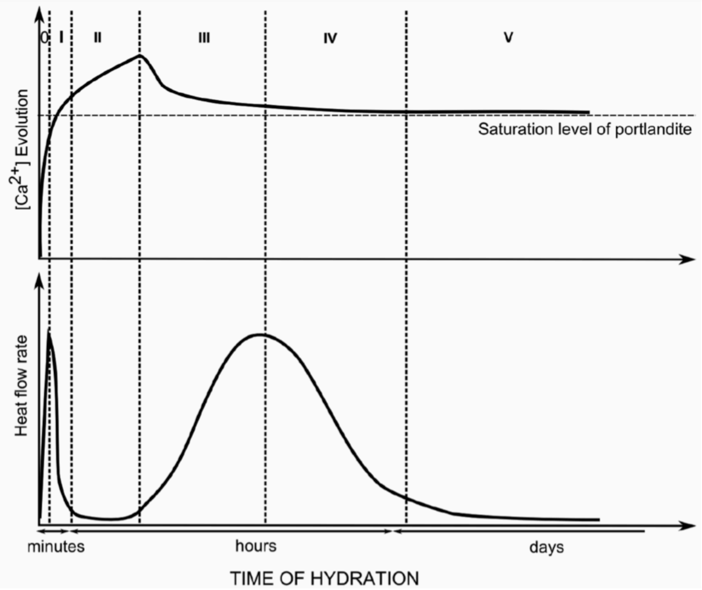

Figure 2-11: Calorimetric curve of alite compared with the saturation level of portlandite [24].

2.2.2 The effect of ZnO in cement hydration

Many researchers have found a retarding effect when ZnO is added directly to cement, caused by the formation of a calcium zincate. Different mechanisms have been proposed through the years, and this section gives a review of the main ones.

In general, zinc behaves differently depending on the pH of the solution. Figure 2-12 shows the different Zn species found at different pH. In cement, the pH range goes from 12 to 13. Therefore, Zn is mainly found as zincate ion $Zn(OH)_4^{2-}$. This Zn species was also observed by Dirkse [25] in alkaline solutions.

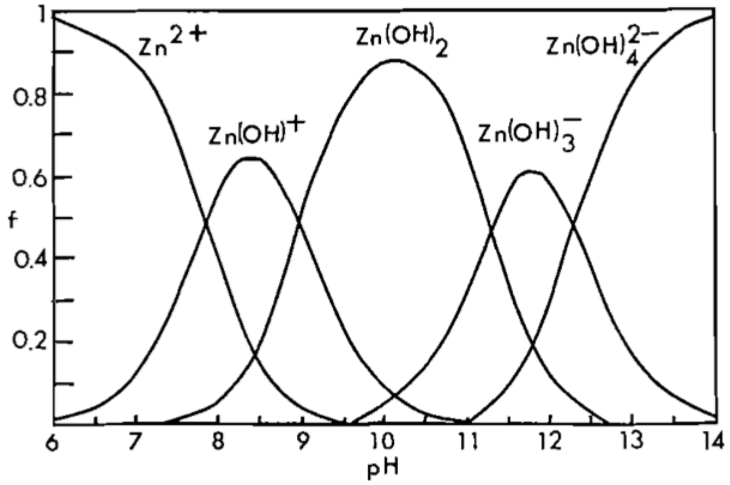

Figure 2-12: Zn species found at different pH at 25 °C [26].

When Ca^{2+} ions exist in solution with zincate ions, calcium zincate ($CaZn_2(OH)_6.2H_2O$) can precipitate according to the next equation:

$$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-} \quad \text{(Eq. 1)}$$

$$Ca^{2+} + Zn(OH)_4^{2-} + H_2O \rightarrow CaZn_2(OH)_6 \cdot 2H_2O + 2OH^- \quad \text{(Eq. 2)}$$

In 1968 W. Lieber [27] carried out interesting work about the influence of Zn compounds on the hydration of Portland cement. Retardation was observed with 0.075% ZnO and the induction period increased with the Zn dosage. Cement with different compositions showed different retardation periods for the same amount of ZnO. The XRD results showed that no portlandite precipitation took place during the induction period, the ZnO peaks decreased in intensity, and a calcium-hydroxo-zincate ($CaZn_2(OH)_6.2H_2O$) appeared. After all the ZnO disappeared, the C_3S reaction took place, and calcium hydroxide precipitated. He concluded that the retardation effect is due to a blocking of the surface of cement grains. Additionally, he studied the hydration of C_3S in the presence of 2% of this Zn salt and observed only slight retardation of the hydration. The XRD showed that the zincate peak decreased during the induction period, and then C_3S reacts, and then the zincate is no longer detectable by XRD. These experiments were reproduced in mortar samples and higher strength was obtained for the samples with calcium zincate. The author related this with the possible incorporation of Zn in the structure of the hydrates, C-S-H, as he reported that long fibrillar structures were seen by SEM in the sample with Zn, and the one with no admixture exhibited more foil-shaped hydrates. He has also stated that for different Zn compounds such as $ZnSO_4$ and $Zn(OH)_2$, the effects were the same as for ZnO.

In the ’80s and ’90s, Arliguie et al. [28] published four papers related to the effect of Zn addition in cement hydration. But the retardation mechanism proposed lacks proof and coherence. In their first research, they studied the retardation effect of Zn in C_3S, C_3A and a mixture between these two phases where the Zn added was 20%, 50%, and 20% respectively. The results are based on XRD and pH measurements. However, no phase quantification was shown, only qualitative data. They concluded that the retardation seen in C_3S with Zn is caused by an impermeable, homogeneous, and amorphous $Zn(OH)_2$ layer that covers the grains, the diffusion of ions is slower, and then the pH of the solution is not high enough for zincate ions to form. Hence, C_3S is retarded as no calcium-zincate is formed. For the C_3A, the fast precipitation of C_2AH_8 on the surface of the grains impedes the formation of a homogeneous $Zn(OH)_2$ layer, and thus the diffusion is less constrained, so the pH increases calcium zincate is formed, and the hydration continues. In the mixed system, the dissolution of C_3A brings Ca^{2+} and OH^- ions into the solution, the $Zn(OH)_2$ layer covering C_3S grains is dissolved, portlandite is precipitated, and the hydration is restarted. They finally concluded that in the presence of Ca^{2+} and OH^- ions decreases the retarding effect of Zn. However, no evidence of the amorphous, homogeneous, and impermeable layer was provided, the Zn source was not mentioned, and the pH measurements of the mixed system were not shown. Therefore, it is difficult to find coherence in their conclusions.

In their second research [29], they studied the hydration of mortars with 0.2-4 wt% of Zn powder by calorimetry. They found higher heat released in stage I for the sample with Zn, and they related it with the formation of $Zn(OH)_2$. No phase was detected by XRD at this point, so they supported the previous hypothesis that $Zn(OH)_2$ is an amorphous compound. The induction period was increased with 0.4% Zn, and the same previous mechanism was proposed to explain this result. Moreover, the main hydration peak was slightly higher for the system with Zn, and this was attributed to the conversion of $Zn(OH)_2$ in calcium zincate and that this crystalline phase can act as nucleation sited for the C-S-H. Again, it is difficult to agree with these conclusions as no evidence of XRD measurements was given, no proof of the amorphous layer, and the calorimetry curve of the system with Zn looks undersulfated.

Their third research [30] was about the influence of different amounts of gypsum on the hydration of cement with 5% Zn. They concluded that 2.5% or less of sulfate is positive to avoid the retardation of Zn. In line with their previous hypothesis, they explained that the C_3A reacts faster and continues to bring Ca^{2+} and OH^- ions to the solution. With more than 2.5% of sulfate, the C_3A hydration is retarded, and therefore the C_3S hydration as well by the amorphous $Zn(OH)_2$ layer.

In their last paper [31], they studied different types of cement and their influence on the hydration in the presence of 5% Zn. They concluded that cement rich in free lime and C_3A reduces the retardation effect of Zn and C_4AF does not affect it. Again, they supported their proposed retardation mechanism with these results, the conversion of $Zn(OH)_2$ to calcium zincate.

Likewise, Asavapisit et al. [32] observed retardation by Zn in cement hydration, and this was attributed to the formation of the impermeable layer. Additionally, they concluded that this layer is not only covering the cement grains but also the gypsum grains hindering its dissolution. They worked with a 10% addition of Zn hydroxide synthetic waste in cement. After 28 days, only unreacted phases were detected by XRD and in their pore solution analysis, after 1 hour of hydration no SO_4^{2-} was present. No evidence of the layer was given.

As discussed in the previous section, Stephan et al. [13] worked with the incorporation of ZnO in the raw material for C_3S synthesis and showed that 2.5 wt% ZnO increases the induction period but also increased the heat released of the C_3S hydration. They concluded that the retardation may be the cause of a Zn salt formation in accordance with Lieber. However, they did not study this in detail and the higher heat released was only mentioned without any explanation.

In more recent years, Trezza et al. [33] showed evidence for the existence of $CaZn_2(OH)_6.2H_2O$ by means of infrared spectroscopy (IR). They used ordinary Portland cement and mixed it with a zinc solution of $ZnNO_3$ with different concentrations of Zn^{2+} in solution, and higher retardation was observed with the increase of Zn^{2+}. Even though no new mechanism was proposed, they mention the previous hypothesis of an amorphous Zn layer inhibiting the hydration until the complete formation of calcium zincate.

It seems that different researchers, in different years, support the hypothesis of the amorphous, impermeable Zn layer covering the cement grains and therefore inhibiting its hydration. However, no evidence for the layer has been given. Therefore, it is necessary to study other possibilities, and as seen in the hydration mechanism section, the initial hydration appears to be controlled by the pore solution and its saturation level. It means that the controlling step here is more chemical than physical as believed in the early years.

Weeks et al. [34] showed with SEM and TEM the non-existence of this coating layer on the cement grains. They defended the idea of retardation caused by the formation of calcium hydroxyl-zincate that consumes calcium and hydroxide ions in the solution and then the time of supersaturation with respect to C-S-H and portlandite is delayed. However, they could not detect calcium zincate with XRD.

Almost ten years later, Ataie et al. [35] concluded that the mechanism behind the retardation effect of ZnO could be a poisoning of C-S-H nucleation and/or growth. Contrary to Arliguie et al. and Weeks et al., their study showed that the concentration of calcium ions during the induction period of samples with Zn is much higher than the reference system after 4 hours from mixing. The concentration of Zn slowly increased until the middle of the induction period because of the dissolution of ZnO and then decreased most probably because of the precipitation of calcium zincate (Eq. 2) or adsorption of Zn in the C-S-H nuclei. They also showed that some SCMs with a high specific surface area can reduce the retardation by Zn as they provide sites for nucleation of C-S-H.

More recently, Matejka et al. [36] studied different Zn sources, $Zn(NO_3)_2$ hydrate, $ZnCl_2$, and ZnO. Even though they did not propose a retardation mechanism, they showed that different Zn sources retard cement hydration. However, the length of the induction period was different with the same amount of Zn, and the best retarder was ZnO due to its lower solubility compared with zinc chloride or zinc nitrate. Nevertheless, no explanation was given.

2.3 ZnO as a potential cement reactivity booster

Apparently, when ZnO forms part of the raw materials and gets incorporated into the crystalline structure of C_3S the heat released is enhanced. This might be due to the low Zn concentrations that are released during alite’s hydration, as proposed previously by Kakali et al. [36] in their hydration study of cement doped with diverse minor elements in the form of oxide. In this case, Zn did not show severe retardation, and the authors attributed this to the slower dissolution of Zn ions when is in the crystal lattice of the clinker phases compared to when Zn is added externally. However, they do not specify in which of the clinker phases Zn is mainly concentrated.

In the same vein, Soga et al. [17] found that a small amount of ZnO (less than 1.91%) in the raw materials increases the heat released and shortens the induction period of the C_3S hydration. With more than 1.91% ZnO white spots were observed in the microstructure and linked with the retardation effect of Zn, but no reason for this was given. They also defend the idea that ZnO changes the reactivity of the C_3A as it is believed that orthorhombic C_3A is more reactive than the cubic and the former was detected in the Zn-doped samples, even though the quantity was reduced.

Gineys et al. [16] concluded that 3 wt% of ZnO can be incorporated in the raw materials as it did not show an important delay in cement hydration. One of the main differences in this research is the synthesis process, where a slow cooling inside the furnace was done aiming to produce bigger alite crystals, but it also influences the elemental distribution. However, they did not explain why Zn had this positive effect.

As proposed by Lieber [27], Zn could be incorporated into the structure of the C-S-H. This could partly explain the hydration curve of alite with the mechanism proposed by Bazzoni et al. [37] In this study, the heat released was doubled with 1.16 and 0.98% ZnO (figure 2-13). This was related to the morphology of the C-S-H; longer needles were observed in the presence of Zn as shown in the STEM images of figure 2-14. Mapping quantification revealed that Zn is homogeneously distributed in the C-S-H structure. Therefore, it suggests that Zn increases the growth rate of C-S-H as it is incorporated into the structure; then, the dissolution of alite is controlled by the C-S-H nucleation and growth, and then, during the deceleration period, the controlling mechanism changes to what is believed the growth of the inner C-S-H (figure 2-15) [22].

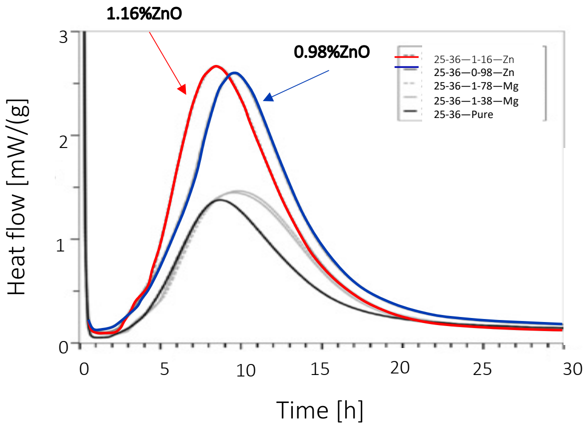

Figure 2-13: The heat flow is enhanced by double with 3% ZnO (1.16% ZnO after evaporation) in the raw materials for C_3S production (modified from [38]).

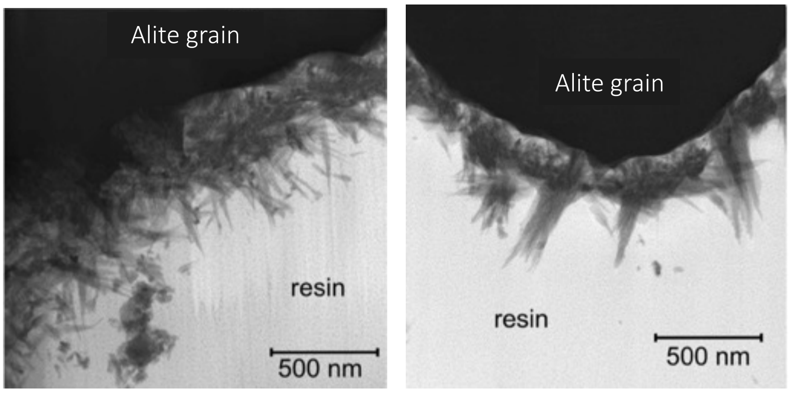

Figure 2-14: Longer C-S-H needles in the presence of Zn (modified from [22])

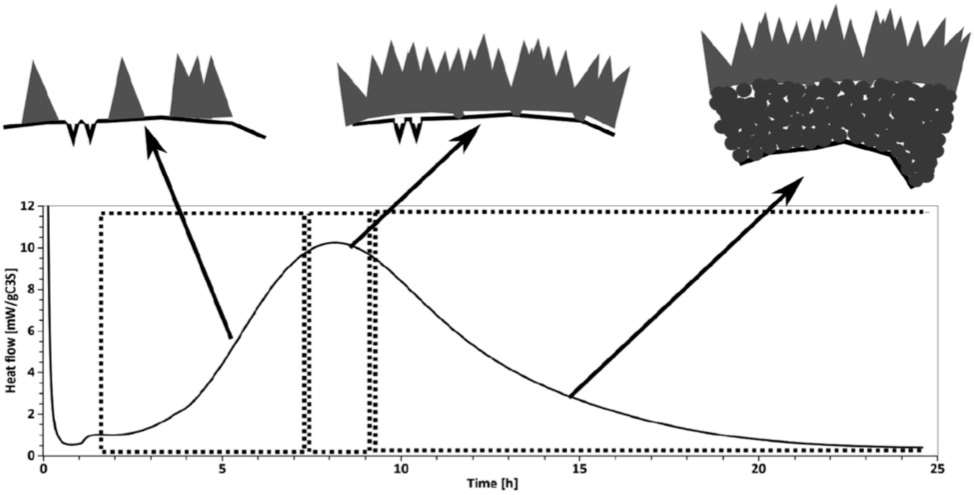

Figure 2-15: The acceleration period is controlled by the growth of the C-S-H needles until no freer surface is available. The transition to the deceleration period is caused by a different growth mechanism since the formation of the inner C-S-H starts [22].

In the same way, the work of Li et al. [39] demonstrates that the incorporation of zinc into C_3S has a very significant effect on early strength. The presence of 0.90% ZnO in C_3S promotes its hydration, and the compressive strength is enhanced until 3 days (figure 2-16). The growth and composition of C-S-H were altered as well, longer needles and clusters were formed in the presence of Zn, in accordance with Bazzoni's results. Also, it was found that most probably the Zn ion is replacing the Si in the tetrahedral chain of the C-S-H structure.

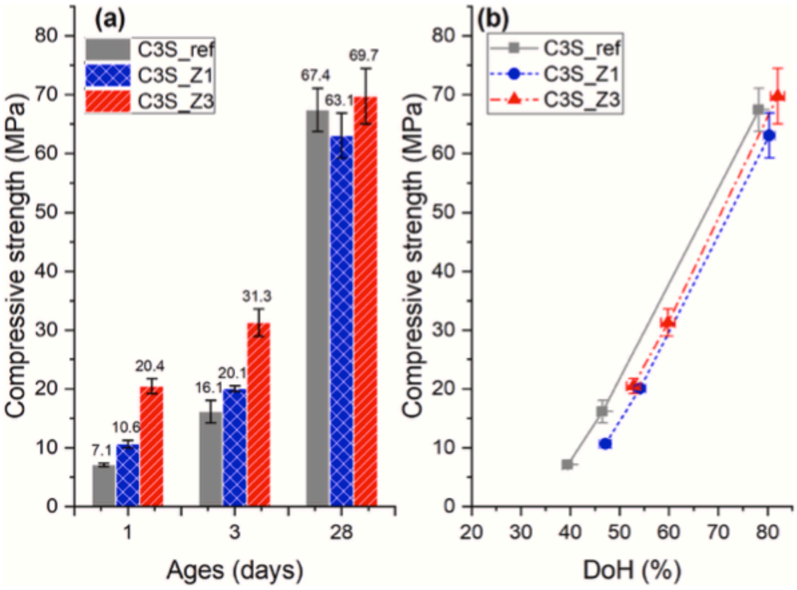

Figure 2-16: Micromortar mechanical test. A) The strength of C_3S with 3%ZnO was 3 times higher than the reference at 1 day and b) the DoH of all samples have a linear relationship with a slight shift between the undoped C_3S and the doped ones [39].

The needle model, developed by Ouzia et al. [40], is a model based on the assumption that C-S-H nucleates and grows as needles in which all the parameters are constrained by experimental data (figure 2-17). They showed that the data from doping experiments made by Bazzoni et al. and Li et al. [37], [39] fit very well with the model simulations. Hence, the needle model supports the hypothesis that part of the hydration peak can be explained in terms of nucleation and growth of needles.

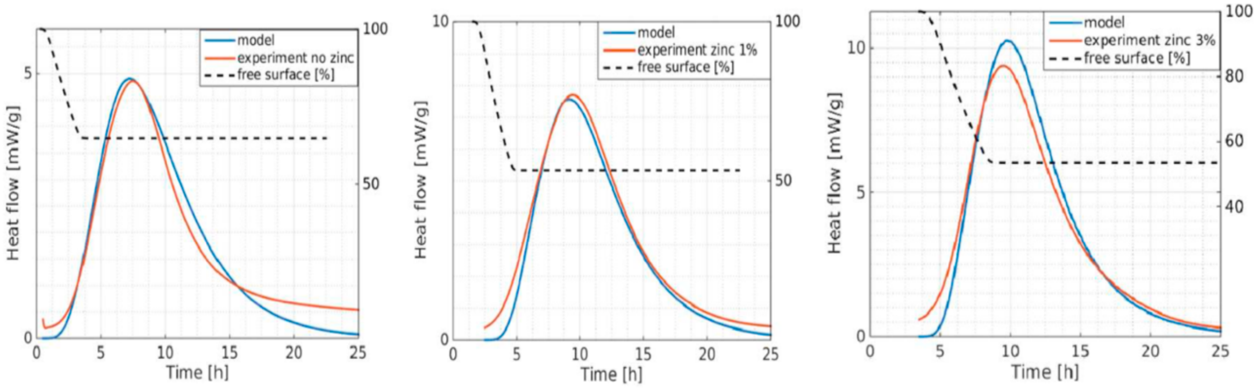

Figure 2-17: Comparison between the experimental data and the needle model [40].

2.4 Conclusions

The retardation effect of Zn at high concentrations has been seen many times. Researchers, who have studied hydration behavior, have proposed several mechanisms. Some of these mechanisms have an experimental backup, and others are pure speculation without any proof. Even though it is important to understand the mechanism behind this effect, little investigation has been made to explain why when Zn is used as part of the raw materials has a positive effect on cement hydration. When the Zn is in the crystal structure of C_3S or alite, the hydration of this phase is enhanced. Most probably because of the small amount of Zn ions released during its dissolution.

What is missing is the link between the effect of Zn in clinker and its effect on hydration behavior as a way to increase the reactivity of the material. This research aims to fill that gap by the study of different ways to make Zn work in real cementitious systems.

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Chapter 3 Effect of ZnO in more realistic systems

Note: this chapter is based on an article in preparation for submission to a peer-reviewed journal.

Contribution of the doctoral candidate: writing of the first manuscript draft, experimental design, conduction of experiments and analysis.

Abstract

Minor amounts of ZnO in the raw materials for C_3S production accelerate the reaction by the incorporation of Zn into the C-S-H structure changing the grow rate of this phase. Longer needles are observed in Zn-doped C_3S. The aim of this work is to understand the effect of ZnO in clinkers (synthesised at laboratory scale) and to investigate the possibilities of enhancing the hydration of these more realistic systems. In C_3A-polyclinker, ZnO promotes the formation of an amorphous phase in which the Zn is mainly concentrated. The reactivity of this phase is higher, and then Zn ions are released faster into solution retarding the hydration, a situation that can be controlled by additional gypsum. No combined ZnO also contributes to the delay. The cooling rate plays a decisive role in the clinkerisation process. Slow cooling is a promising solution to retain more Zn in the alite phase, to obtain less amorphous, and enhance the reactivity of more realistic systems.

Contents

3.1 Introduction

The use of concrete is expected to increase in the following years as the worldwide population increases. However, the cement industry contributes 5-8% of the anthropogenic CO_2 emissions [1]. Environmentally, it is necessary to reduce concrete's impact. In cement manufacture, Portland cement clinker can be partially replaced with supplementary cementitious materials (SCMs) such as industrial wastes and by-products. This replacement lowers the CO_2 emissions as less clinker is used. However, this substitution reduced the low early age strength.

There are different approaches to address this problem. One of them is the study of clinker chemistry to make a better and more reactive clinker. Recent works [2][3] showed that by adding ZnO in the raw material, Zn gets incorporated into the crystalline structure of the C_3S. Then, during the hydration, a higher rate of reaction is observed during the main heat evolution peak. This enhancement was related to longer C-S-H needles where Zn was found to be incorporated, seen in the scanning transmission electron microscopy (STEM) and leading to higher mechanical strength at early ages.

Although the mechanisms behind this effect are not well understood yet, it indicates that ZnO has the potential to increase cement reactivity and allow higher substitution levels of cement by SCMs. Even though C_3S is the pure primary clinker phase, Zn has a different effect in real clinker. As ZnO is added as raw materials, it is essential to understand the clinkerisation process and its clinker chemistry. This subject has been studied for a long time ago but with different focus and conclusions through time. Some researchers [4][5] state that ZnO acts as a mineralizer, promoting the formation of clinker phases at a lower temperature and that it also changes the properties of the C_3A.

Other authors [6], have proven that the formation of a new phase composed of aluminum, zinc, and calcium is possible, as seen later by Barbarulo et al. [7] and Gineys et al. [8]. Despite the different conclusions, they agree that Zn is mainly concentrated in the interstitial material and that retardation is observed after a certain dosage is exceeded. However, very limited research has been conducted to understand the mechanism behind the retardation and propose solutions to mitigate it.

With the focus on Bazzoni's hypothesis [2] that Zn in C_3S structure enhances hydration, this research aims to understand the different effects in more realistic systems and look at ways to avoid the retardation effects. The effect of ZnO in raw material for two systems is discussed in this paper, alite as the impure form of C_3S and a synthetic polyclinker to consider a more realistic situation. The phase quantification, study of microstructure and Zn repartition, and the reactivity in terms of alite dissolution were studied by X-ray diffraction (XRD), scanning electron microscopy coupled with EDX (SEM-EDX), and isothermal calorimetry, respectively. In addition, to better understand the clinkerisation process, differential scanning calorimetry (DSC) was used, and the different transition temperatures were compared. Finally, a new hypothesis is provided to explain the effect of ZnO in more realistic systems and solutions with the potential for further reduction of the environmental impact of cementitious materials.

3.2 Materials and Methods

3.2.1 Materials

Two different systems were synthesized in the laboratory using high-purity chemicals. The first one is alite, where the mix composition was taken from Taylor's Cement Chemistry book [9], with MgO, Al_2O_3, and Fe_2O_3 as impurities (table 3-1). The second system corresponds to a C_3A-Polyclinker in which the same mix composition was used, but more calcium and alumina were added to obtain 90% alite and 10% C_3A. These two systems were doped with 1, 3, and 5 wt% of ZnO, as seen in table 1. Two extra dosages of ZnO were tested to find the quantitative limits in the alite system only. However, this investigation is focused on 1, 3, and 5 wt% ZnO.

Table 3-1: Mix design for the two systems studied, alite and C_3A polyclinker.

System	**Sample**	**Nomenclature**	**Raw materials (%)**					
			CaO	**SiO_2**	**Al_2O_3**	**MgO**	**Fe_2O_3**	**ZnO**
Alite	Alite	A	70.55	26.82	0.74	1.16	0.73	0.00
	Alite 1%ZnO	A1	69.84	26.55	0.73	1.16	0.72	1.00
	Alite 3%ZnO	A3	68.43	26.02	0.72	1.13	0.70	3.00
	Alite 5%ZnO	A5	67.02	25.48	0.70	1.11	0.69	5.00
C_3A-Polyclinker	Polyclinker	P	69.56	24.14	4.60	1.06	0.64	0.00
	Polyclinker 1%ZnO	P1	68.86	23.89	4.55	1.05	0.65	1.00
	Polyclinker 3%ZnO	P3	67.47	23.41	4.46	1.03	0.63	3.00
	Polyclinker 5%ZnO	P5	66.08	22.93	4.37	1.00	0.62	5.00

The calcium carbonate is from VWR, the SiO_2 silica fumed from Sigma-Aldrich with a particle size Dv_{50} of 0.007 µm, the aluminum, magnesium, and zinc oxide from MERK, and the iron oxide (99.999%) from Acros Organics.

3.2.2 Synthesis Process

The synthesis was carried out following the method developed by Li et al., illustrated in figure 3-1. The raw materials were mixed in a mill jar for 24 hours. The raw mix was composed of 750 grams of powder mixed with 1500 grams of water (water/material = 2). The next step was to cast this mix into cylinder moulds and dry at 100 °C in an oven. After drying, they were calcined at 1600 °C for 3 hours with a heating rate of 7 °C/min. Finally, the material obtained was ground in a disc mill to get the powder for its characterization. For the slow cooled synthesis, the samples were kept inside the furnace (OFF) until 1250 °C and then cooled down by air with a fan. The cooling from 1600 °C to 1450 °C takes approximately 20 min.

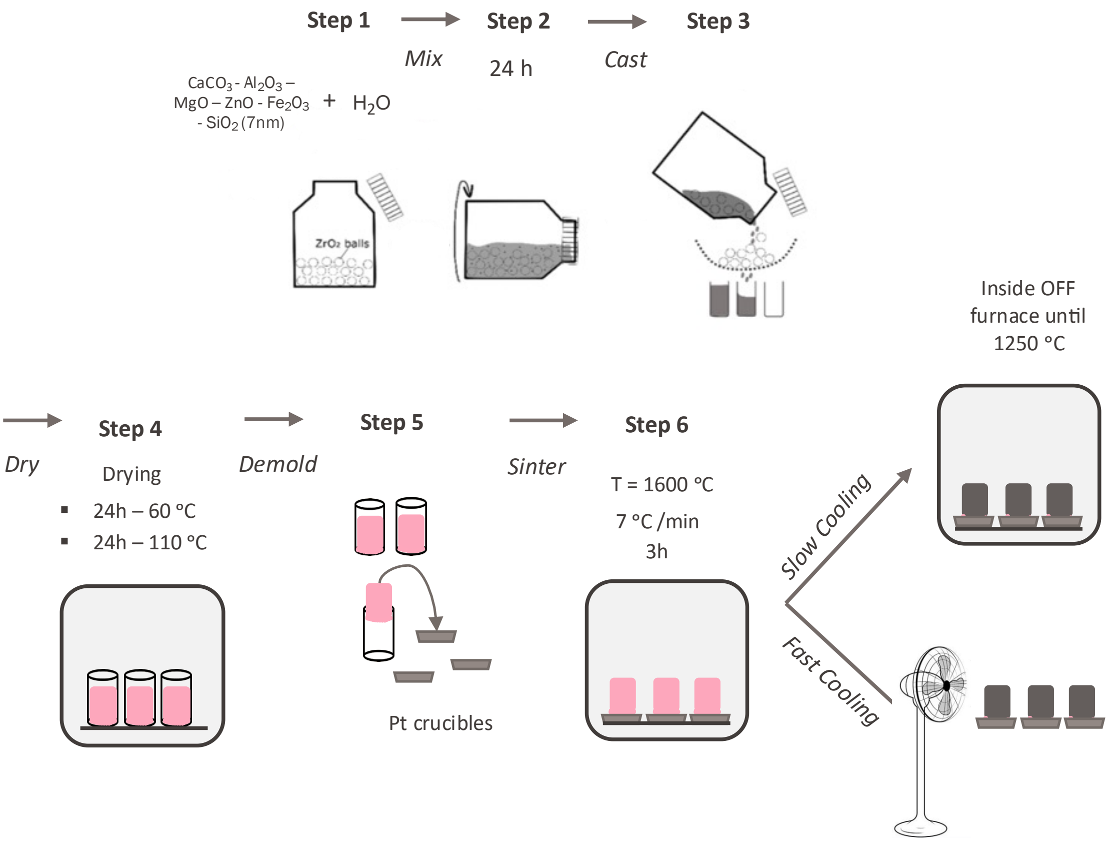

Figure 3-1: Synthesis process for alite and C_3A-polyclinker (modified from [2]).

3.2.3 Characterization methods

Isothermal calorimetry at 20°C was used to evaluate the hydration behavior of the samples. First, the powder samples were mixed with water at a solid ratio of 0.5 for 2 min with a speed of 1600 rpm. Second, 10g of paste were placed into glass ampoules which were then closed. Then, the ampoules were filled and placed inside the calorimeter. The data were acquired and analyzed for two weeks. For the polyclinker system, the samples were mixed with 5% gypsum to control the C_3A reaction.

To verify the quality of the systems produced by phase quantification and detect if Zn formed new phases, X-Ray Diffraction (XRD) measurements were done in an X'Pert MPD PRO diffractometer with CuKα radiation at 45 kV and 40 mA. The diffractograms were collected from 5 to 70° 2θ. To minimize the absorption contrast that affects the peak intensities, the powder samples were previously ground with a McCronizer mill [9]. Thus, 5 g of powder and 10 mL of isopropanol was ground for 5 min. The amorphous content was quantified with the external standard method (rutile, TiO_2).

For the alite system, the composition in terms of oxides was obtained by X-Ray Fluorescence (XRF). The measurements were done externally by Thermo Fisher Scientific, Chemin de Verney 2, 1024 Ecublens. The particle size distribution (PSD) was measured by laser diffraction with a Malvern MasterSizer S with the SHE_3 optical model (n=1.7, k=0.1, n=1.39). The specific surface area was determined by Brunauer–Emmett–Teller 5 points method (SSA-BET), where the nitrogen adsorption-desorption was obtained with a Tristar II plus from Micromeritics.

The microstructure and morphology evolution were studied by scanning electron microscopy (SEM). The samples were prepared, and the hydration was stopped by the isopropanol exchange method. For backscattered electron imaging in the scanning electron microscope (SEM-BSE), the dried samples were impregnated in resin, polished, and coated with carbon. Unhydrated powder was also prepared in the same way. An FEI Quanta 200 microscope operating at 15 kV was used. For secondary electron imaging (SEM-SE), the samples were crushed, spread on a conductive tape, and then coated with 7nm of Iridium. In this case, a Zeiss Merlin microscope was used.

Scanning transmission electron microscopy (STEM) was used to obtain high-resolution images in an FEI Technai Osiris (FEI CO, Hillsboro, OR) to measure the C-S-H needle length and compare alite without doping and alite with 3%ZnO.

3.3 Effect of ZnO in alite and C_3A-polyclinker

3.3.1 Alite

The calorimetry curves in figure 3-2 show an enhancement in heat released when alite is doped with ZnO, and this effect is roughly linear up to 4% ZnO. More ZnO added to the raw materials causes severe retardation of alite hydration (figure 3-3), similar to what other researchers have seen when ZnO is added as an additive [10]–[12].

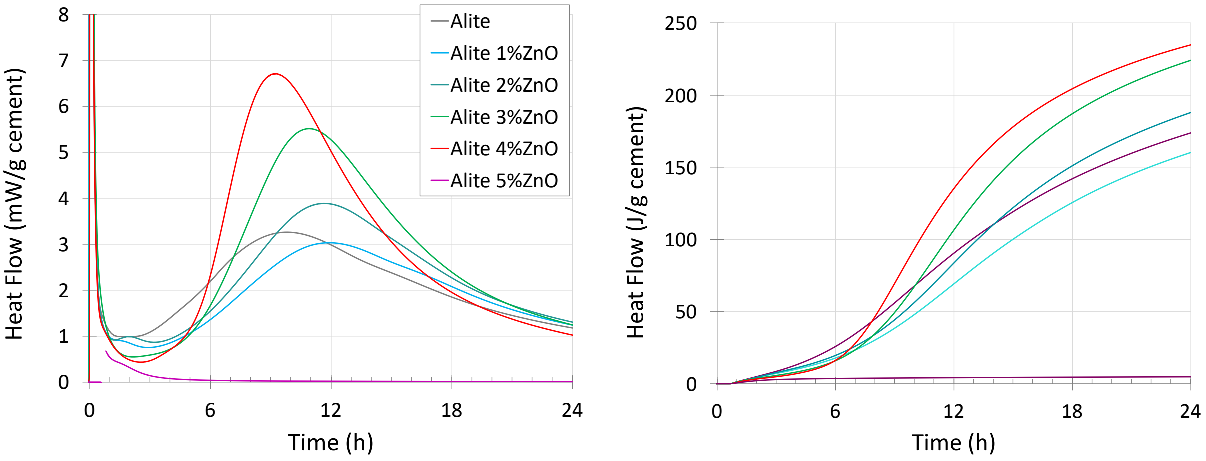

Figure 3-2: Calorimetry curves for alite system doped with ZnO: reactivity enhancement up to 4 wt% ZnO.

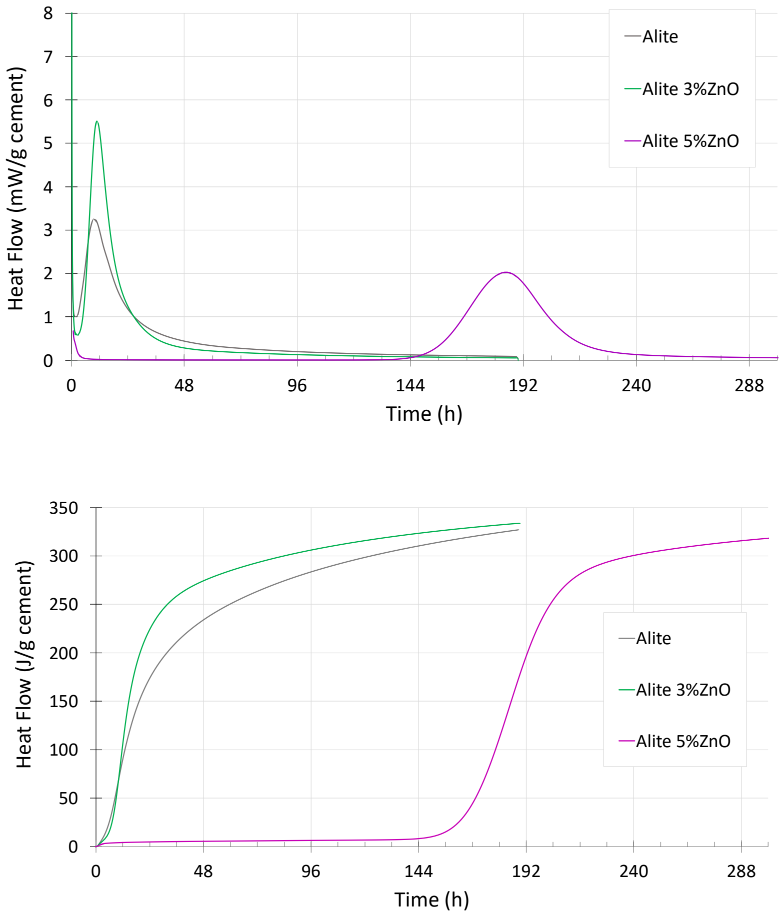

Figure 3-3: Calorimetry curves for alite system doped with ZnO: severe retardation is observed with 5 wt% ZnO.

Table 3-2 shows the XRD – Rietveld quantification in which no “free ZnO” was detected nor any other phase with Zn. No trend is seen for the free lime, and the lowest amount was detected for alite doped with 5% ZnO. Hence, there must be some joint substitution of calcium and silicon by zinc. However, this is an indirect indication that must be further investigated.

In addition, the type of polymorph can be identified with the angular window shown in figure 3-4. The presence of two or three peaks in the ranges 32-33° and 51-53° can indicate whether the alite has a monoclinic or triclinic structure. In comparison with literature, alite with 3% of ZnO and without doping has an M3 structure [9]. When the dosage of ZnO is increased to 5%, the peaks start to deform, and their shape suggests a combination of polymorphs between M1 and M3. Further, the peaks are slightly shifted, which means that zinc can probably go into the crystalline structure of alite, changing the lattice dimensions. Therefore, it is highly probable that Zn is incorporated in alite structure.

Table 3-2: Phase quantification and oxide composition of alite system doped with ZnO.

System / Phase (%)	**C_3S**	**Free lime (CaO)**
Alite	98.9	1.1
Alite 3% ZnO	97.9	2.1
Alite 5% ZnO	99.7	0.3

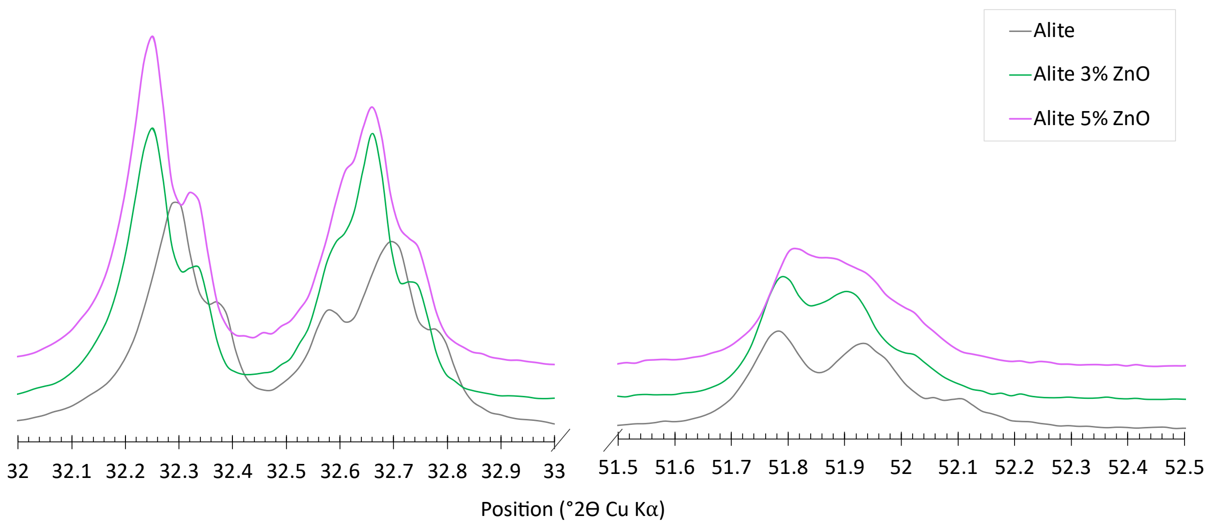

Figure 3-4: The angular window for the polymorph identification showing a tendency for a combination of M1 and M3 in the alite doped with 5% ZnO.

Another important observation is the XRF results of alite system (table 3-3) compared with the C_3S doped with Zn taken from [2] and [3] seen in table 3-4 and 3-5. They found that part of the zinc evaporates during the calcination process for the C_3S synthesis, but less ZnO is evaporated in the alite system. Hence, it seems that the evaporation of ZnO can be minimized in the presence of the other minor elements, Al, Mg, and Fe.

Table 3-3: Oxide composition of alite system

System / Oxide (%)	**CaO**	**SiO_2**	**MgO**	**Al_2O_3**	**Fe_2O_3**	**ZnO**
Alite	70.88	24.37	1.17	0.70	0.76	0.00
Alite 1%ZnO	70.70	24.50	1.16	0.70	0.72	0.62
Alite 3%ZnO	69.63	24.06	1.08	0.63	0.66	1.90
Alite 5%ZnO	67.01	23.26	1.06	0.77	0.68	4.98

Table 3-4: Oxide composition of C_3S system taken from Bazzoni's et al. work [2].

System / Oxide (%)	**CaO**	**SiO_2**	**MgO**	**ZnO**
Pure C_3S	72.80	24.47	0.00	0.23
Alite 1.5% wt Mg	70.98	24.68	1.38	0.08
Alite 2% wt Mg	70.58	24.62	1.78	0.00
Alite 3% wt Zn	72.27	4.46	0.00	0.98
Alite 4% wt Zn	71.57	24.62	0.00	1.16

Table 3-5: Oxide composition of C_3S system taken from Li's et al. work [3].

System / Oxide (%)	**ZnO**
C_3S_ref	0.00
C_3S_Z3	0.90

Moreover, it was found that the particle size increased as the amount of ZnO increased (table 3-6), even when the grinding process was the same for all the samples. In other words, the grindability is changed with zinc dosage as the grains are harder to grind. The roughness of the grains was also affected by ZnO. Grains are rougher as more ZnO is added, significantly for the 5%ZnO system (table 3-6). Accordingly, the grains are bigger but with a higher specific surface area that can also affect the hydration behavior. Even so, the enhancement observed can not be exclusively caused by this effect.

Table 3-6: Particle size and specific surface area of alite doped with ZnO.

	Alite	**Alite 1%ZnO**	**Alite 3%ZnO**	**Alite 5%ZnO**
Dv_{50} (μm)	9.08	11.92	12.49	18.88
SSA (m^2/g)	0.88	0.96	1.04	1.70

The higher heat released can be related to the microstructure of the hydrated grains and morphology of the C-S-H as reported previously for the pure C_3S phase doped with ZnO. The microstructure of the reference and the sample with 3%ZnO can be compared in figure 3-5. Even though both systems are at 24 hours of hydration, the one with ZnO shows more hydration products and 'Hadley grains.' These grains react completely, leaving a ring of C-S-H with a space inside, for smaller grains, or a space between the ring and the grain, for bigger grains [13]. This suggests that the reaction occurred faster in the sample with ZnO than in the reference one.

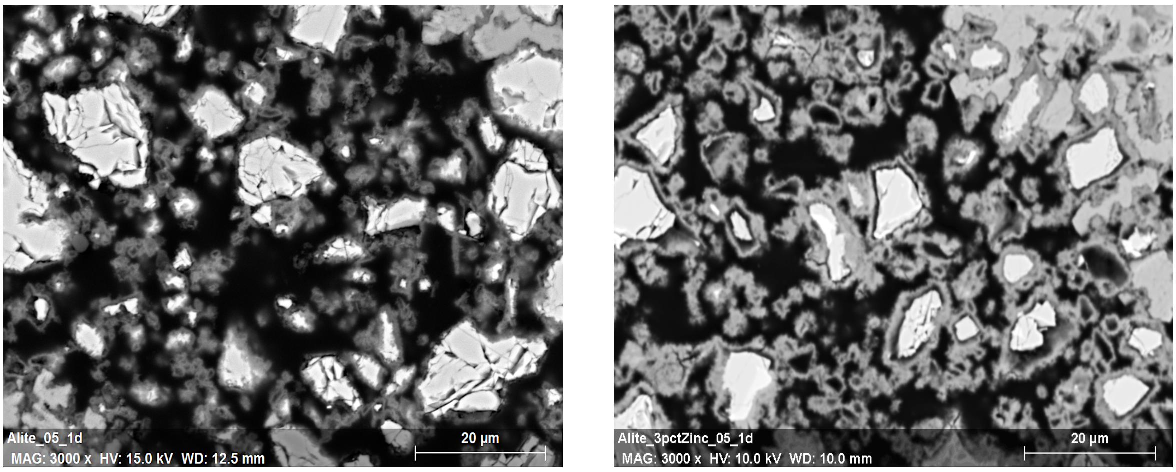

Figure 3-5: Microstructure after one day of hydration with a w/c=0.5. Left: Alite and right: Alite doped with 3%ZnO.

A closer look at the morphology of the main hydration product, C-S-H, by SEM-SE is shown in figure 3-6. The reference alite shows a C-S-H with a crumpled sheet-like structure, while the doped system is more similar to a needle-like one. Together with the TEM images in figure 3-7, longer needles are observed when the sample is doped with ZnO, which is in accordance with the observations for pure C_3S. These results support Bazzoni's hypothesis [2] that the acceleration period is controlled by the growth of the C-S-H.

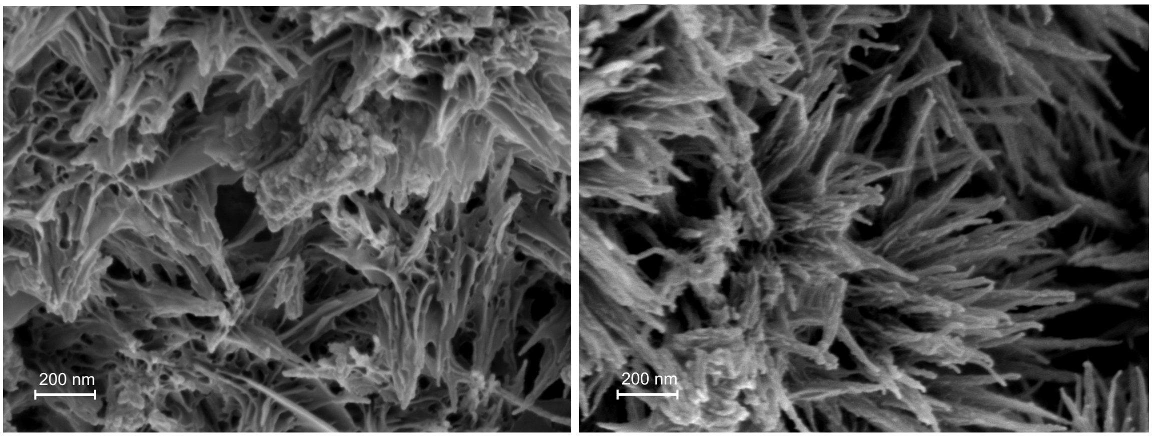

Figure 3-6: C-S-H morphology at 1-day, left: alite and right: alite doped with 3%ZnO.

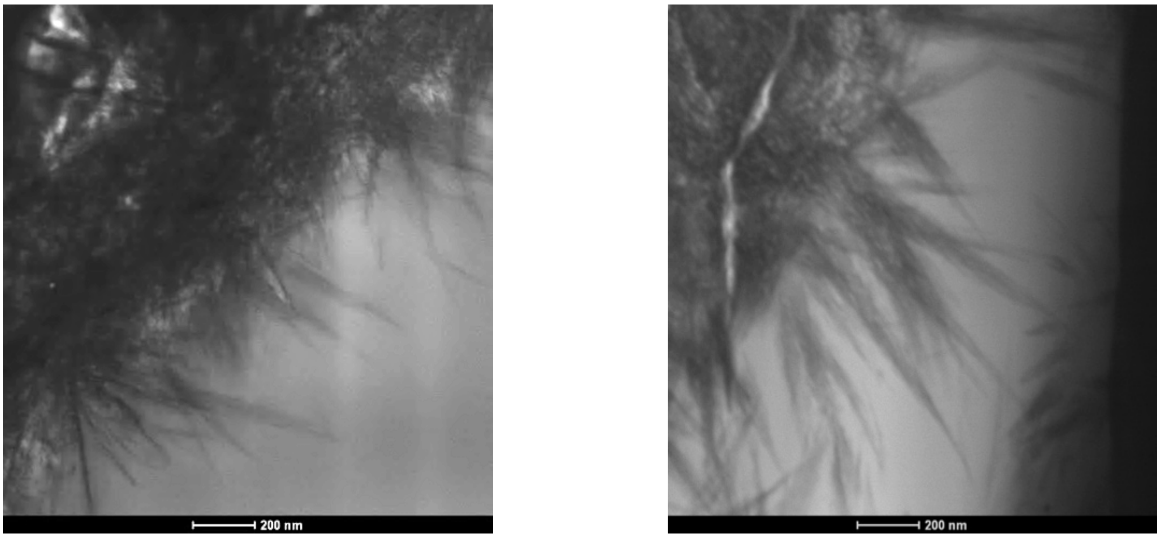

Figure 3-7: C-S-H needles of left: alite and right: alite 3%ZnO at one day of hydration.

The incorporation of Zn in the C-S-H structure is believed to be responsible for the increase in the needle length, as Zn was detected in the SEM-EDX results seen by Bazzoni. et al. [2]. Further research is needed to verify it.

3.3.2 C_3A-Polyclinker

Figure 3-8 shows the calorimetric curves for the polyclinker system intended to be 90% alite and 10% C_3A doped with ZnO. A significant difference is observed compared to alite behavior previously discussed (figure 3-2). In this case, there is an increase in the induction period, and this effect is roughly linear with the ZnO dosage added to the raw materials.

This retardation was also observed in real clinker systems previously investigated by [14][15]. To understand the reasons for this difference exists compared to the alite, it is necessary to find out where the Zn going in the more realistic system.

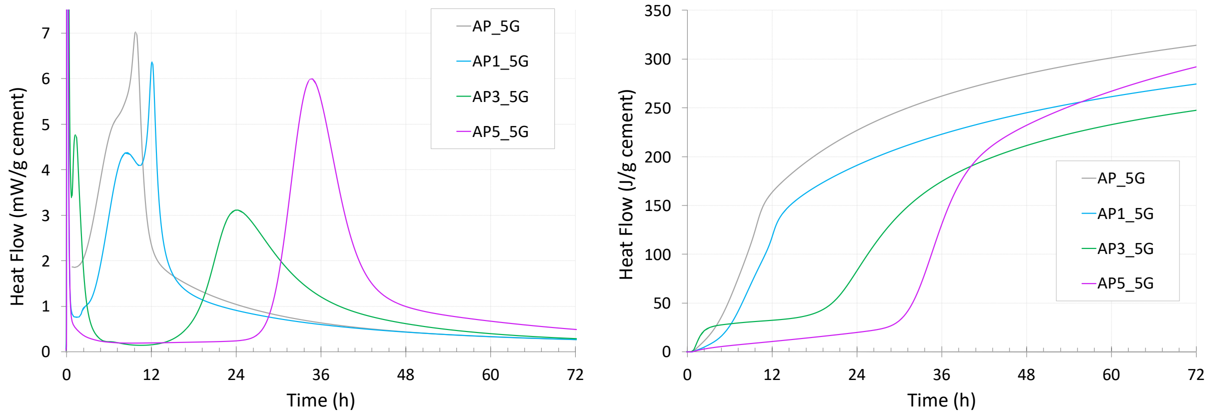

Figure 3-8: Calorimetric curves for C_3A-polyclinker (AP) system doped with ZnO with 5% of gypsum addition.

In table 3-7, the phase quantification estimated by Rietveld is shown. It was found that when the ZnO dosage increases, less C_3S is formed. Besides, the C_3A decreases and changes from cubic to orthorhombic when 5%ZnO is added, which is a more reactive [16]. Moreover, with a higher ZnO in raw materials, more amorphous phase is formed at the expense of C_3S and C_3A.

Table 3-7: Phase quantification of C_3A-polyclinker system doped with ZnO.

System/Phase (%)	**C_3S M3**	**C_2S**	**C_3A - C***	**C_3A - O****	**Free lime (CaO)**	**Zincite (ZnO)**	**$MgFeCaSiO_3$**	**Portlandite**	**Amorphous**
P	78.30	5.40	8.90	-	1.80	-	-	-	5.60
P1	76.700	0.00	7.31	-	-	-	-	-	16.00
P3	76.50	0.50	3.70	0.10	-	0.50	-	-	18.70
P5	60.60	1.90	-	1.80	0.10	1.00	1.70	4.80	27.70

* C_3A cubic

**C_3A Orthorhombic

With regards to the PSD and the SSA, little can be concluded from the measurements (table 3-8). In alite, Zn seems to lower the grindability of the particles, but there is a higher SSA. In the polyclinker case, these effects are not seen. Compared to the reference polyclinker, the doped samples show larger particle sizes and lower SSA. However, again, the results in figure 3-9 cannot be explained by means of PSD and SSA only.

Table 3-8: Average particle size and specific surface area (SSA) of C_3A-polyclinker (AP) doped with ZnO (AP1 = 1%ZnO, AP3 and AP5 respectively).

	AP	**AP1**	**AP3**	**AP5**
Dv_{50} (µm)	17.16	21.10	20.89	19.34
SSA (m^2/g)	1.10	0.60	0.64	1.00

Another way to answer where the Zn is going in these systems is by the analysis of the microstructure by SEM coupled with EDX to estimate the amount of Zn in each phase. Figure 3-9 shows a typical microstructure of a grain from the polyclinker with 5%ZnO. The darkest areas correspond to alite crystals; the next one in the grey level is free lime. The lightest area is the interstitial material, in this case, is composed mainly of aluminum and minor amounts of magnesium and iron. Using EDXIA, it was found that Zn prefers to stay in this interstitial material where the other minor elements are remaining in alite.

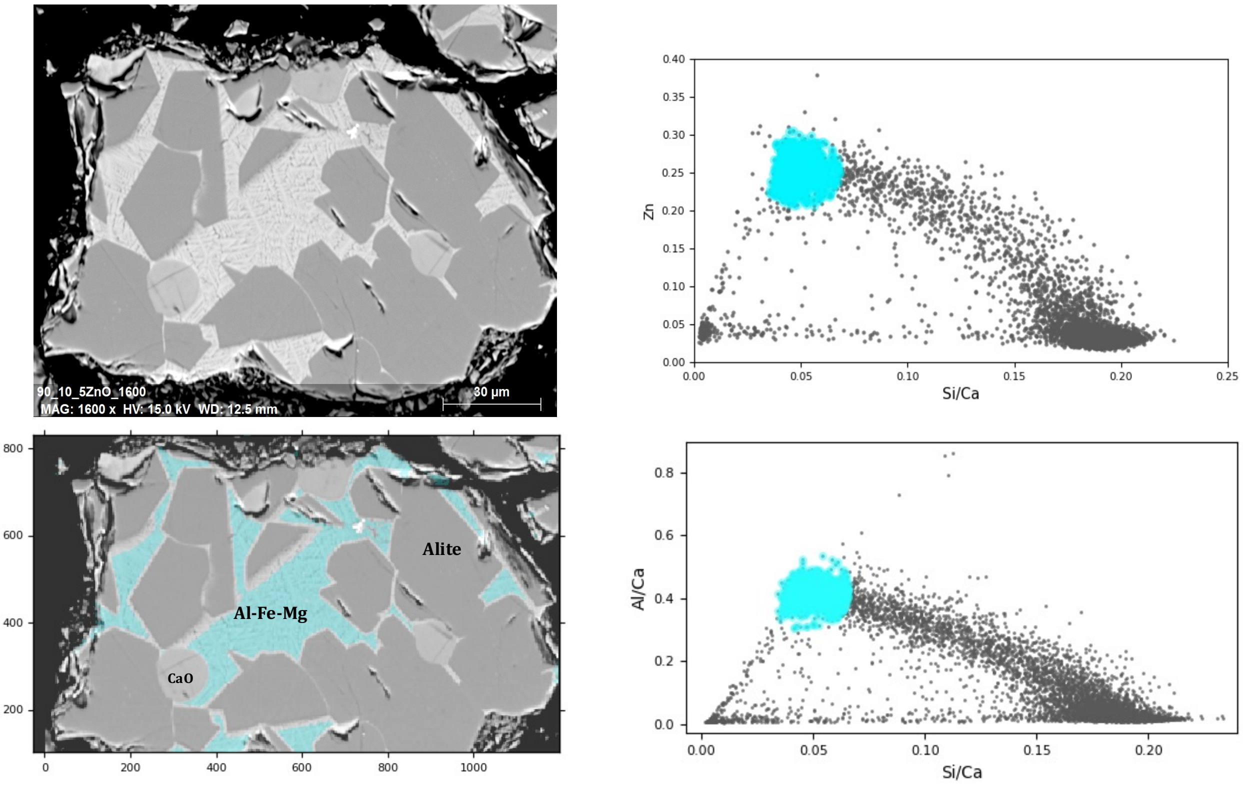

Figure 3-9: Phase distribution of a polyclinker 5%ZnO grain showing that Zn is concentrated in the interstitial material.

Moreover, together with the XRD results (table 3-7) and knowing that the interstitial material come from the recrystallized liquid that forms during the clinkerisation process, it is possible to say that the presence of Zn inhibits its crystallization.

Based on the SEM and XRD results, it is concluded that: *Zinc is mainly concentrated in the amorphous phase. As its dissolution is fast, there is a rapid release of Zn ions to solution retarding alite reaction.* Subsequently, as the amorphous corresponds to the alumina-containing material, it can be supposed that more gypsum can be added to control its dissolution and avoid Zn release. Figure 3-10 shows the effect of

10% gypsum in the polyclinker with 5%ZnO, where the alite peak is shifted to the left and maintains the same heat release as the control.

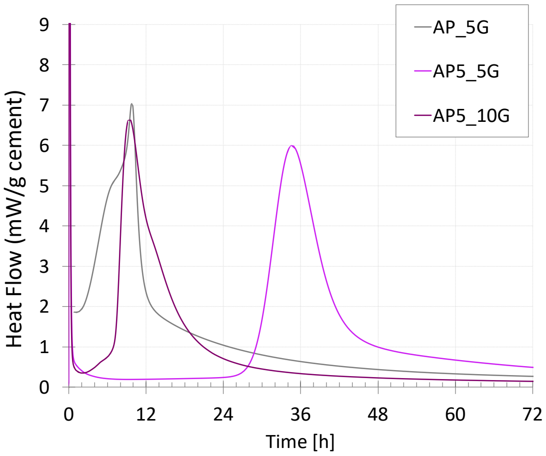

Figure 3-10: Sulfation correction of polyclinker 5%ZnO with 10% of gypsum.

To sum up this section, a potential explanation for the differences between alite and polyclinker, both doped with ZnO, is the Zn repartition. Zn in alite works up to 4% ZnO, and in the more realistic systems, Zn is mainly concentrated in the other phases changing the hydration behavior. In polyclinker with a high amount of C_3A, Zn promotes an amorphous phase that dissolves fast and retards alite hydration. Adding more gypsum controls the reaction of this phase. The next step was to investigate if it is possible to make Zn work in more realistic systems by retaining it in the alite phase.

3.4 Study of possible solutions to make ZnO work

3.4.1 Effect of ZnO in the C_3A-Polyclinker interstitial material

The interstitial material of polyclinker without and with 5% ZnO was reproduced from the elemental composition obtained by SEM-EDX. The same synthesis process was followed, and the same raw materials were used. Figure 3-11 shows the product after calcination of the two interstitial materials. The sample with ZnO has a glassier appearance than the reference one, typical for amorphous phases. The brown color comes from the Pt dissolution in the melt, 200 ppm measured by ICP by A. Pisch (private communication).

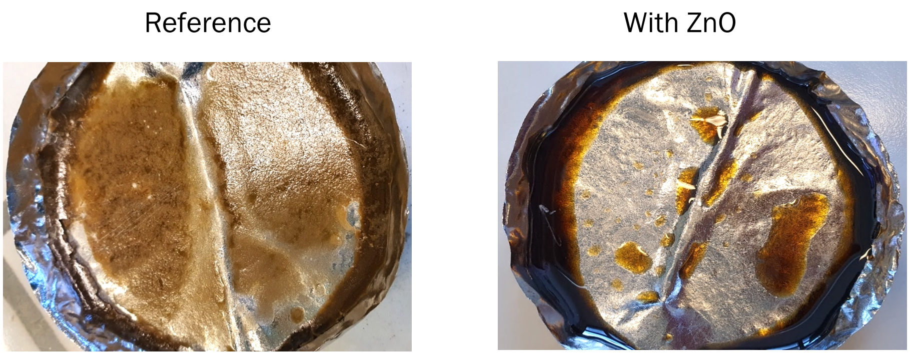

Figure 3-11: Interstitial material after calcination.

This observation is confirmed by the XRD results (figure 3-12), showing no crystalline peaks for the sample with ZnO, only an amorphous hump. On the contrary, some peaks are found in the diffractogram of the reference system. These peaks correspond to cubic C_3A, portlandite, and free lime.

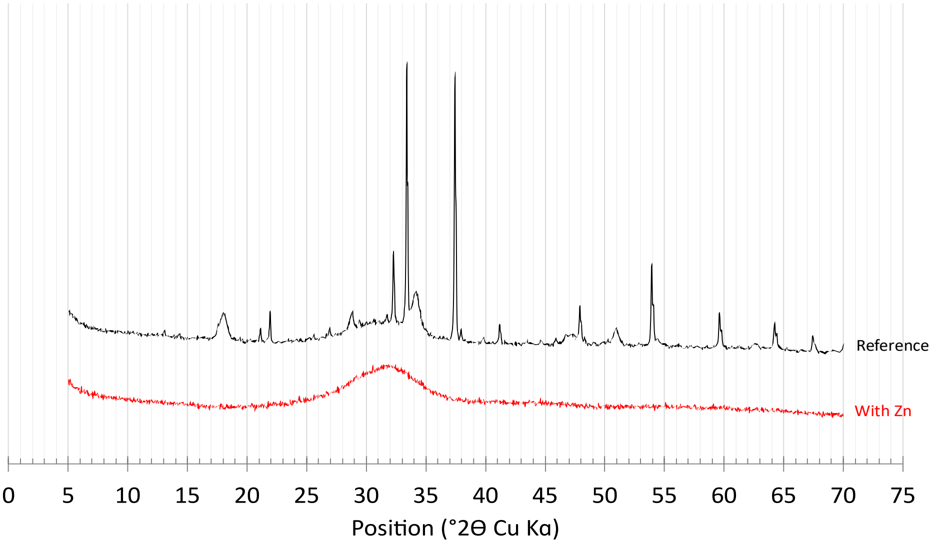

Figure 3-12: XRD comparison between interstitial material with and without Zn.

Furthermore, the reference sample has different microstructures, as seen in figure 3-13. Some grains have a dendritic microstructure indicating crystallization. However, the grains in the sample with Zn are entirely uniform, confirming once more an amorphous phase (figure 3-14).

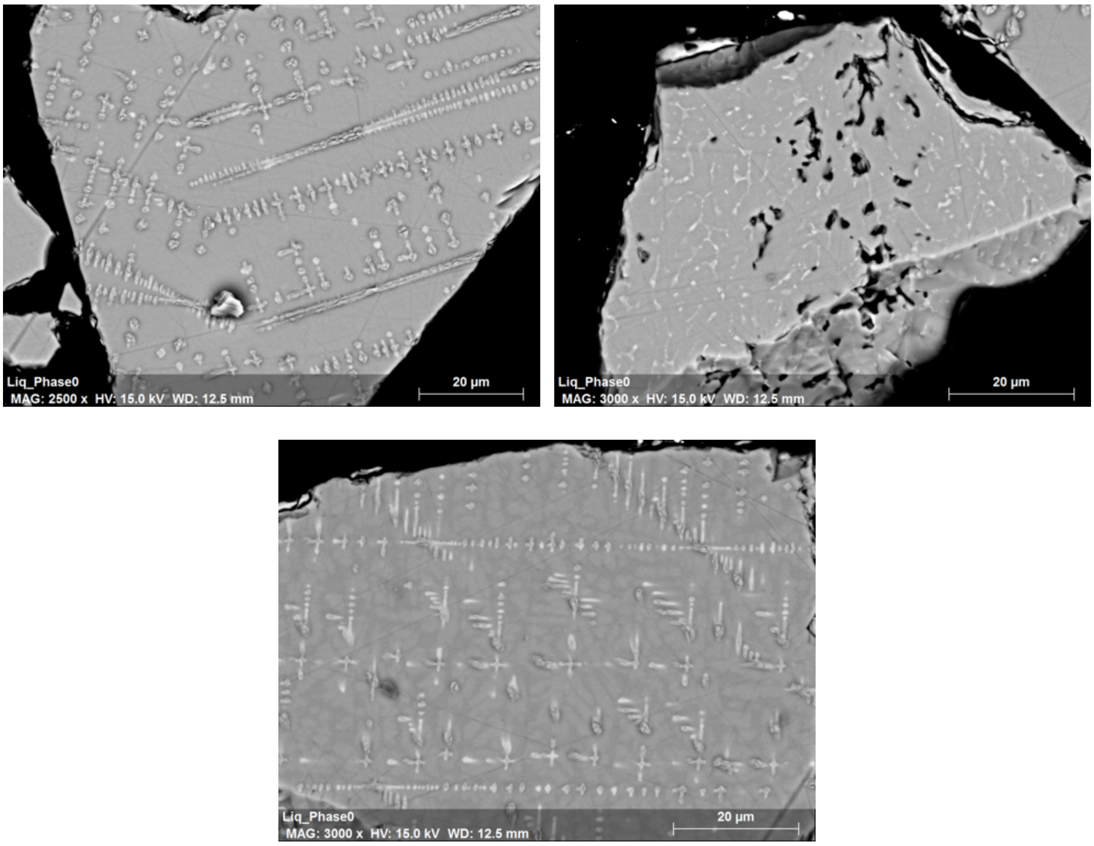

Figure 3-13: Microstructure of the reference interstitial material without doping.

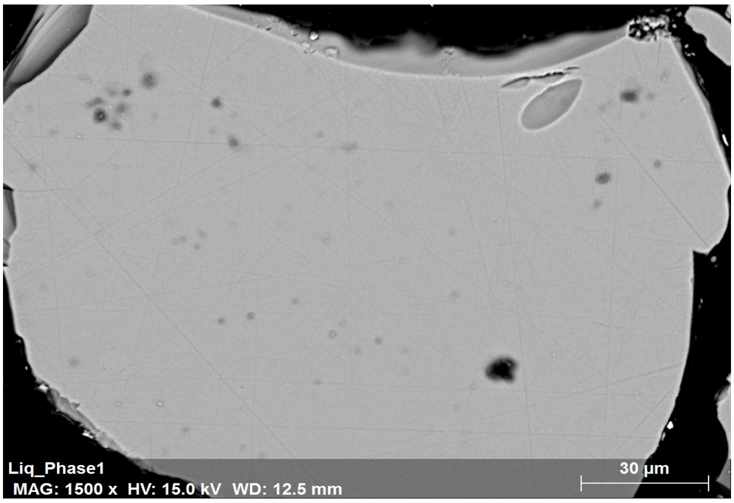

Figure 3-14: Microstructure of the interstitial material with Zn.

3.4.2 Strategies to retain zinc in alite: slow cooling to 1250°C

The polyclinker with 5%ZnO was again synthesized following the same process except for the quenching at the end. In this case, a slow cooling was studied by keeping the samples inside the furnace until 1250 °C, and then taken out and cooled down by air with a fan. The quenching was done from 1250 °C to avoid the conversion of alite to belite.

The phase quantification is shown in table 3-9, and figure 3-15 shows the Zn repartition between the two cooling rates for the polyclinker with 5% ZnO. A slow cooling promotes the C_3S phase, and the amorphous content is considerably lower. Moreover, there was found to be more Zn in the alite than in the quenched sample.

Table 3-9: Phase quantification of the C_3A-Polyclinker doped with 5% ZnO, fast and slow cooled.

System/Phase (%)	C_3S M3	C_2S	C_3A-C	C_3A-O	Free lime (CaO)	Zincite (ZnO)	$MgFeCaSiO_3$	Portlandite	Amorphous
P5	60.60	1.90	0.00	1.80	0.10	1.00	1.70	4.80	27.70
P5_SC	75.20	2.80	3.03	0.00	0.99	0.52	0.00	1.02	16.00

It is important to notice here that 0.64 % of Zn in alite for the polyclinker fast cooling could explain why, in figure 3-8, a higher heat released is observed for 5 wt% ZnO compared to the reference system, even when is retarded. In this case, the uncombine ZnO could be the cause of the delay, while the increase in heat is caused by the Zn in alite.

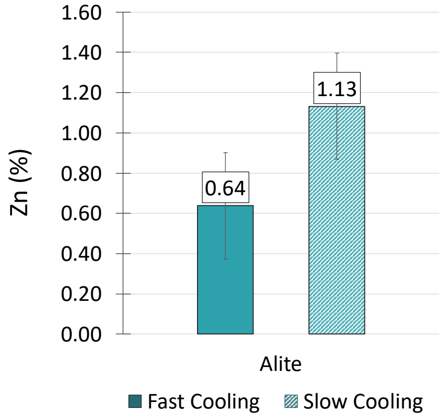

Figure 3-15: Zn repartition in alite of polyclinker doped with 5% ZnO when is fast and slow cooled.

With the previous results and considering our main hypothesis that Zn in alite increases its reactivity, it was expected that the hydration of the slowly cooled samples should be enhanced. This enhancement can be observed in figure 3-16. Even though there is slight retardation in the first 6 hours, the heat released increases afterward.

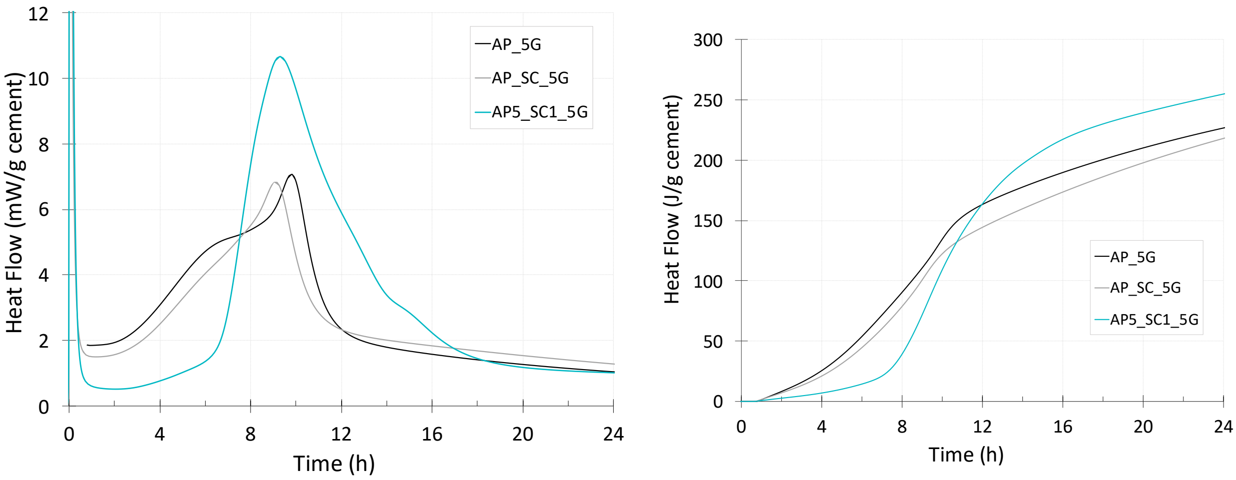

Figure 3-16: Calorimetric and cumulative curves for polyclinker 5%ZnO slow cooled with 5% gypsum (AP5_SC_5G). Comparison with reference system fast (AP_5G) and slow cooled (AP_SC_5G).

In this case, only 5% of gypsum was sufficient to control the C_3A reaction, most probably because a less amorphous phase was formed. This also supports the assumption that the interstitial material in the quenched sample could be amorphous based on aluminate material, with a faster dissolution rate, which needs more gypsum to control its hydration.

To study the reproducibility of the slow cooling rate system, two more samples were prepared and analyzed in the same way. Figure 3-17 shows that the enhancement is reproducible, normalizing the calorimetry curves by the specific surface area (table 3-8). However, an increase in the induction period is observed. The difference in the roughness of the grains is believed to be associated with the grinding process. Although it was the same process, the amount of material between the discs in the disc mill could not be the same for each sample, affecting the final roughness.

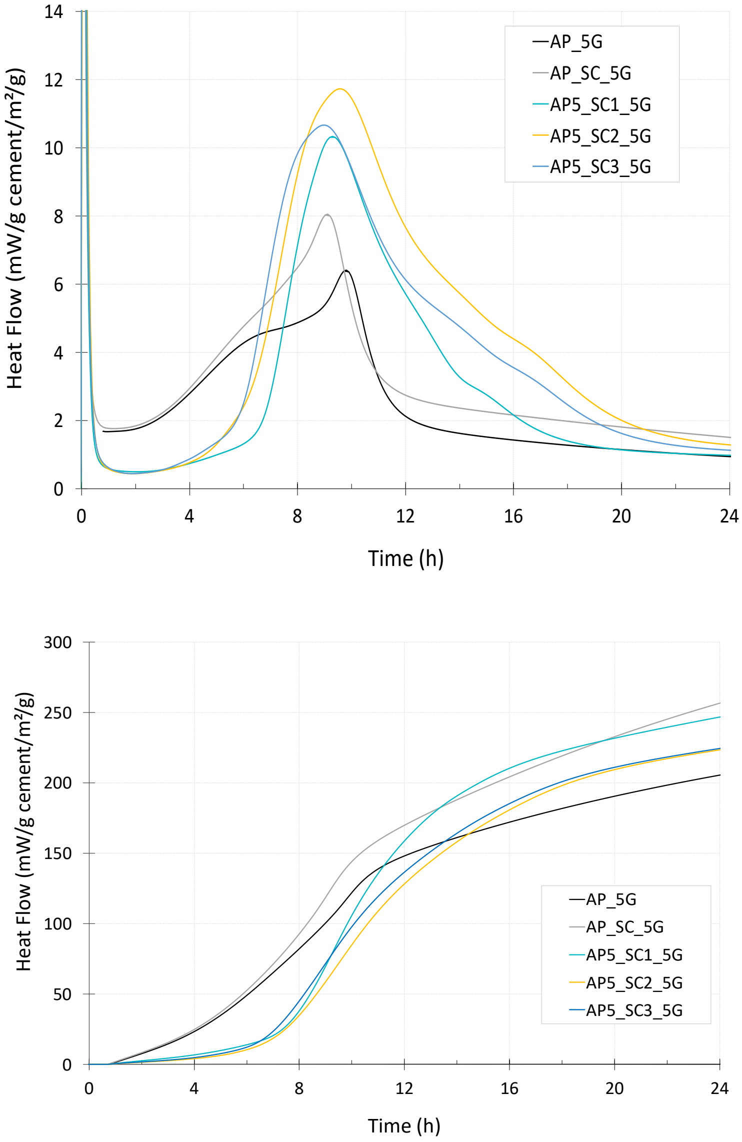

Figure 3-17: Calorimetric curves for three batches of polyclinker 5%ZnO (AP5) slow cooled with 5% gypsum. Comparison with reference system fast and slow cooled.

Table 3-10: Average particle size and specific surface area (SSA) of polyclinker 5%ZnO (AP5) slow cooled (SC) and comparison with the three batches (SC1, SC2 and SC3).

	AP	**AP_SC**	**AP5_SC1**	**AP5_SC2**	**AP5_SC3**
Dv_{50} (μm)	17.16	19.09	20.86	20.83	16.66
SSA (m^2/g)	1.40	0.85	1.03	0.63	0.71

The Zn repartition for the three batches can be seen in figure 3-18. The amount of Zn in alite is very similar to the slowly cooled samples, demonstrating that the enhancement observed in the hydration could be, in fact, due to the effect of Zn in alite.

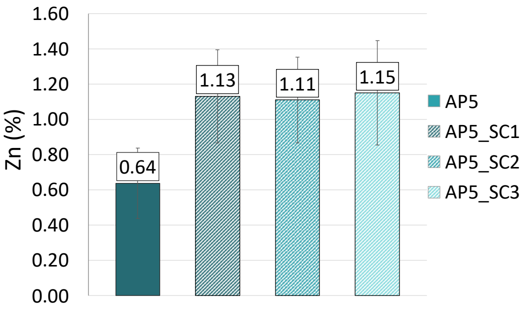

Figure 3-18: Zn repartition for polyclinker system. Comparison with different batches and cooling rates.

These results represent potential solutions for the application of ZnO as raw materials. Slow cooling can be implemented in the industry by changing the position of the flame. It can be placed to the front a little, so the thermal shock between the kiln and the clinker cooler is less. This will allow more time for ions to redistribute in the clinker phases. However, it is fundamental to continue with further investigations to understand better the role of Zn in clinker chemistry and hydration.

3.5 Conclusions

Minor amounts of ZnO, up to 4 wt%, in the raw materials enhance alite reactivity similarly to pure C_3S. This can be attributed to the incorporation of Zn in the C-S-H structure, promoting its growth as longer needles were observed. More than 4 wt% of ZnO leads to severe retardation associated with the uncombined ZnO.

In a C_3A polyclinker, ZnO lowers the early age properties and promotes the formation of an amorphous phase in which the Zn is mainly concentrated. Its rapid reaction releases Zn ions in solution, and thus retardation is observed. An additional amount of gypsum can avoid this situation. However, these effects still agree with the central hypothesis that the dissolution of alite releasing Zn enhances

The cooling rate has a decisive role in clinkerisation with doping ions. With a slow cooling rate, more alite and less amorphous were formed. At the same time, more Zn was retained in the alite phase as the ions in the liquid phase have more time to get a better distribution. This resulted in a more reactive polyclinker than the reference one, and the enhancement is reproducible if the specific surface area is considered. These results show that a slow cooling rate is a promising solution to retain more Zn in the alite phase, obtain less amorphous, and enhance the reactivity of more realistic systems.

The increase of the induction period needs further investigation, as well as the differences in the interstitial material at the microscopic and compositional levels to better understand the effect of Zn in this phase. On the other hand, the amorphous content seems to be an important variable in the extension of the induction period. Hence, the study of alternatives to slow cooling that decreases its content and promote more Zn in the alite phase could help to reduce the induction period.

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Chapter 4 Study of the retention of Zn in alite

Note: this chapter is based on an article in preparation for submission to a peer-reviewed journal.

Contribution of the doctoral candidate: writing of the first manuscript draft, experimental design, conduction of experiments and analysis.

Abstract

The hydration of alite is enhanced with up to 4% ZnO addition in the raw materials for its synthesis. In polyclinker systems, the addition of ZnO has a retarder effect as the Zn repartition is different and it is mainly concentrated in the interstitial material or as free ZnO that remained uncombined. A slow cooling rate after the calcination procces promotes a better distribution of Zn, increases its concentration in the alite phase and enhances the hydration of these systems. This study aims to investigate ways to retain more Zn in alite in polyclinker systems and its effect on hydration given its potential to increase the reactivity of cementitious systems. With a recalcination of the C_3A-polyclinker doped with ZnO, a change in the interstitial material to C4AF, and a decrease in the amount of interstitial material to 5%, more Zn was found in the alite phase. However, the amorphous content and the free ZnO seem to be more dominant in terms of hydration kinetics as longer induction period were observed. Moreover, a severe retardation was found when gypsum was added to the C_4AF-polyclinker systems.

Contents

4.1 Introduction

The previous chapter showed that up to 4% of ZnO increases the heat released in alite. On the contrary, a more realistic system, such as a polyclinker composed of 90% alite and 10% C_3A, when doped with ZnO, shows retardation. The difference is due to the Zn repartition. In the alite one-phase system, Zn is incorporated in the crystalline structure of alite, supporting our hypothesis that Zn in alite enhances the reactivity by its slow Zn release to solution as alite reacts, and the incorporation of Zn in the C-S-H structure [1][2]. In the polyclinker system, Zn is mainly concentrated in the interstitial material, composed of the aluminate phase. The amorphous content increases as the ZnO dosage increases, which is related to the aluminate phase [3][4]. Therefore, Zn affects the thermodynamics of the synthesis process, as previously seen by other researchers [5]–[8]. With a slow cooling, it was possible to get more Zn in the alite and less amorphous content. This was translated into higher heat released, supporting our hypothesis. Even though the slow cooling process has potential to be implemented in the industry, other potential ways to make Zn work in more realistic systems must be investigated. In this section, different approaches to retaining more Zn in alite are investigated: recalcination of the C_3A-polyclinker, effect of C_4AF as the interstitial material, and lower amount of interstitial material.

4.2 Materials and methods

4.2.1 Raw materials, mix design and synthesis process

Three different polyclinker systems were synthesized in the laboratory with the mix design in table 4.1. For the recalcination study, a polyclinker designed to be 90% alite and 10% C_3A was prepared, without doping and with 5% ZnO. This dosage of ZnO was chosen to study the case with the highest amorphous content found. For this study, the insterstitial material of the C_3A-Polyclinker doped with 5% ZnO was synthesized. The mix design was based on the composition of this interstitial material obtained by scanning electron microscopy coupled with energy dispersive X-ray (SEM-EDX) point analysis and is shown in table 4-1. The second system corresponds to a 90% alite and 10% C_4AF polyclinker. The Al_2O_3/Fe_2O_3 was decreased to a minimum of 0.64 to promote the formation of C_4AF over C_3A [4]. For the third system, the A/F ratio was kept at 0.64, but the proportions of raw materials were changed to get a polyclinker with 95% alite and 5% C_4AF.

The synthesis process followed the method developed by Li et al. [9] and as shown in figure 3-1 from the previous chapter. The raw materials were mixed with water in a zirconia milling jar for 24 hours and then cast into cylinder mould made of carton. The mix was slowly dried in a 60 °C oven for 1 day and then changed to a 110 °C oven for a total water evaporation for another day. Then, the cylinders samples were demoulded, placed in platinum crucibles, and placed inside an 1800 °C furnace (Borel Swiss). The calcination was done at 1600°C at a rate of 7 °C/min, retained for three hours, and then cooled down by air with a fan. The recalcination was done at 900 °C for 30 min using the same furnace, crucibles, heating, and cooling rate.

Table 4-1: Mix design for C_3A (AP), C_4AF (FP) polyclinker systems, and the interstitial material of C_3A-polyclinker system doped with 5% ZnO.

System/ Raw materials (%)	**CaO**	**SiO_2**	**Al_2O_3**	**MgO**	**Fe_2O_3**	**ZnO**
AP	69.56	24.14	4.6	1.06	0.64	0.00
AP_5ZnO	66.08	22.93	4.37	1.00	0.62	5.00
Interstitial	43.88	3.24	30.62	4.33	4.15	13.78
FP	66.50	23.83	3.11	1.72	4.85	0.00
FP_1ZnO	65.84	23.59	3.08	1.70	4.8	1.00
FP_3ZnO	64.51	23.12	3.02	1.67	4.7	3.00
FP_5ZnO	63.18	22.64	2.95	1.63	4.61	5.00
5FP	69.00	25.56	1.5	1.56	2.34	0.00
5FP_3ZnO	66.97	24.79	1.46	1.51	2.27	3.00

For the C_4AF-Polyclinker, the same synthesis process was followed but with some modifications. As the liquid phase forms at around 1338 °C in a pure system with ferrite [4], [10], the calcination was done at 1450 °C with the same speed and retention time. Additionally, before placing the samples in the furnace, the cylinders were split into small pieces to avoid any damage to the furnace from a possible liquid phase (figure 4-1). The effect of the cooling rate was also studied for this system, where the samples were kept in the furnace until 1250 °C and then cooled down by air with a fan. After calcination, the samples were ground by hand, micronized, and stored under vacuum for its characterization.

Figure 4-1: Sample preparation for the synthesis of C_4AF-Polyclinker. From left to right: cylinders divided into small pieces, placed into platinum crucibles, and the sample after calcination.

4.2.2 Experimental methods

Differential scanning calorimetry measurements were done to study the transition temperatures of the interstitial material in the C_3A-Polyclinker. The equipment was a NETZSCH DSC 404C, and platinum crucibles were used with an outer diametr 6.8 mm, one for the reference and other for the sample. Both crucibles were weighted together with the lid, and then 37.300 mg of the interstitial material, previously ground by hand, was added. The reference sample was kept empty. The system was purged with argon three times previous the test which was designed to go up to 1200 °C with a heating rate of 10 °C/min and an argon flow rate of 50 ml/min. After the experiment, the data was analyzed with Proteus software

The C_3A-Polyclinker was ground with a disc mill. 100 g of material were added and each ground for 60 seconds. The C_4AF-Polyclinker (10 and 5% C_4AF) was manually ground with a stainless-steel mortar. Both systems were ground again with a McCrone micronizing mill for XRD examination. For this, 5 g of sample were mixed with 10 ml of isopropanol, ground for 5 minutes, and then the mix was filtered to get the powder. The samples were kept under vacuum to avoid contamination or moisture reaction.

The composition of the powders was obtained by X-ray driffraction (XRD) with a X'Pert MPD PRO diffractometer with CuKa radiation at 45 kV and 40 mA. Back loading holders were used. The diffractograms were collected from 5 to 70° 2θ and analyzed with HighScore software with Rietveld refinement.

Laser diffraction was used to measure the particle size distribution (PSD) with a Malvern MasterSizer S with the SHE_3 optical model (n=1.7, k=0.1, n=1.39). The specific surface area was determined by nitrogen adsorption-desorption obtained with a Tristar II plus from Micromeritics following the Brunauer–Emmett–Teller 5 points method (SSA-BET).

Scanning electron microscopy (SEM) coupled with energy dispersive X-ray (SEM-EDX) was used to analyze the microstructure of the polyclinker grains and quantify the amount of Zn in alite. The powder was impregnated in resin, polished, and coated with carbon. The equipment used was a FEI Quanta 200 microscope with a back-scattered electrons (BSE) mode and operating at 15 kV. The morphological study was done with a Zeiss Merlin microscope using the secondary electrons (SE) detector. The powder samples were spread on conductive tape and coated with 7 nm of Iridium.

Finally, the hydration was followed by isothermal calorimetry at 20 °C. The sample was first mixed with distilled water with a water to solid ratio of 0.5 for 2 min with a speed of 1600 rpm with an IKA eutostar 40 mixer. Then, 10 g of the mix was rapidly introduced into glass ampoules, closed, and placed inside the calorimeter. The experiment was done in a control temperature room at 20 °C. For the AP, FP reference, and 5FP reference, 5% gypsum was added to control the aluminate reaction. The Zn-doped FP and 5FP systems were mixed without gypsum, and the reason will be exposed in the following sections.

4.3 Results of the three approaches to retain Zn in alite

4.3.1 Recalcination of the C_3A-Polyclinker

The C_3A-polyclinker showed an increase in the amorphous content with the dosage of ZnO in the raw materials. Therefore, the synthesis process, and more specifically the cooling process allows neither the crystallization of the interstitial material nor a better ion distribution in the clinker phases. Hence, Zn is trapped in the uncrystallized interstitial material and not in the alite. Consequently, Zn ions are fast released into the solution and retard the hydration of alite. A recalcination of the system permits us to investigate if its recrystallization releases the Zn and if it goes to the alite.

Differential scanning calorimetry measurements were done with the synthesized interstitial material of the C_3A-polyclinker 3%ZnO to determine the crystallization temperature of this phase. The glass transition can be seen in figure 4-2 at 722.0 °C to 747.3 °C, confirming the amorphous nature of this phase. Moreover, there two exothermic peaks corresponding to the crystallization (847.6 °C and 876.6 °C) and after the melting (1272 °C). Thus, this phase is crystalline from 900 °C until melting at 1240 °C. Consequently, the heat treatment was carried out at 900 °C for 30 minutes using the same furnace and platinum crucibles.

The recalcination produced more C_3S and less amorphous compared to the reference system (table 4-2). However, more C_2S and free CaO were detected in the recalcined sample. Since the amorphous phase consists mainly of calcium, aluminum, and zinc, this suggests that recalcination makes more calcium available for the formation of C_2S, and CaO, and the presence of Zn could promote the formation of more C_3S under these conditions. The Zn that was not incorporated into the clinker phases remained as free ZnO. On the other hand, the recalcination had little effect on the C_3A content.

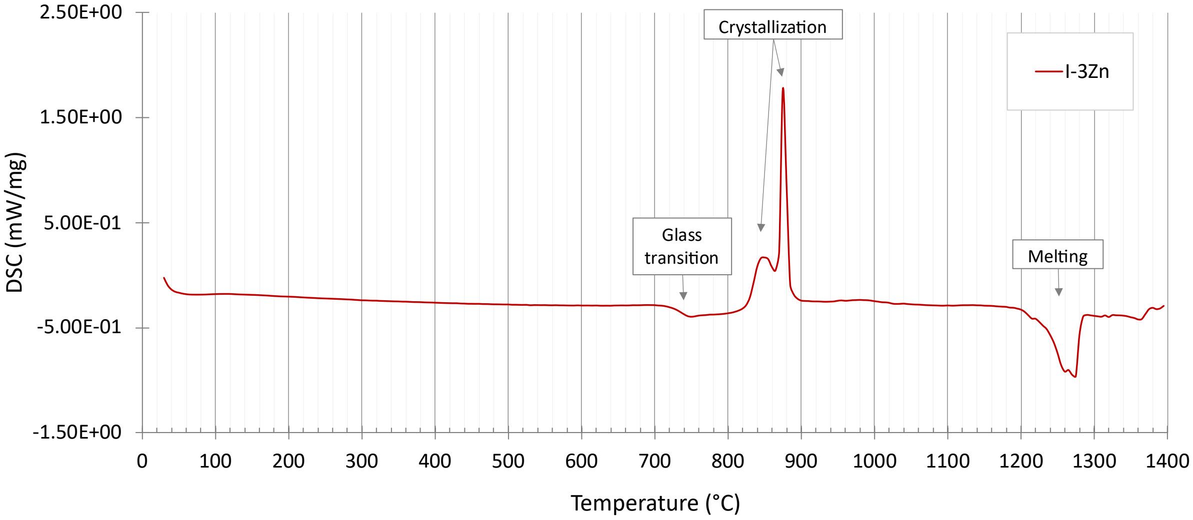

Figure 4-2: DSC curve for the synthesized interstitial material for the C_3A-polyclinker doped with 3%ZnO.

Table 4-2: Phase quantification of C_3A-Polyclinker, reference and recalcined.

Phase (%) / Sample	**C_3A-Polyclinker 5%ZnO**	
	REF	**Recalcined**
C_3S (M)	76.40	79.90
C_2S	0.94	3.90
C_3A	2.95	2.65
CaO	1.26	2.78
ZnO	0.44	0.60
Amorphous	18.00	10.20

Moreover, figure 4-3 compares the microstructure of the two systems. The interstitial material of the reference system is composed of three different microstructures: 1) dendritic 2) interstitial A 3) interstitial B with dark and white spots, similarly, as seen in the previous chapter. The recalcined sample exhibited mainly a dendritic interstitial material, but an interstitial material A was also found. The latter is related to the amorphous phase, and the fact that less is seen in the recalcined sample is consistent with the XRD quantification, as less amorphous was detected. In addition, the crystal size of alite appears to be larger than in the reference system.

Edxia was used to analyze the elemental mappings of the microstructures in figure 4-3, and the same chemical composition was found for the interstitial materials, dendritic, interstitial A, and B. The difference relies in how the phases inside are distributed. The interstitial A resulted a phase with a lower C/A ratio than C_3A, and the interstitial B was a combination of C_3A and interstitial A (figure 4-4). As can be seen in figure 4-5, the concentration of Zn increases with Al content, but decreases with the type of microstructure, from a) and b) to c) in figure 4-3. The thermally treated sample shows the same observations for the interstitial A and the dendritic microstructure.

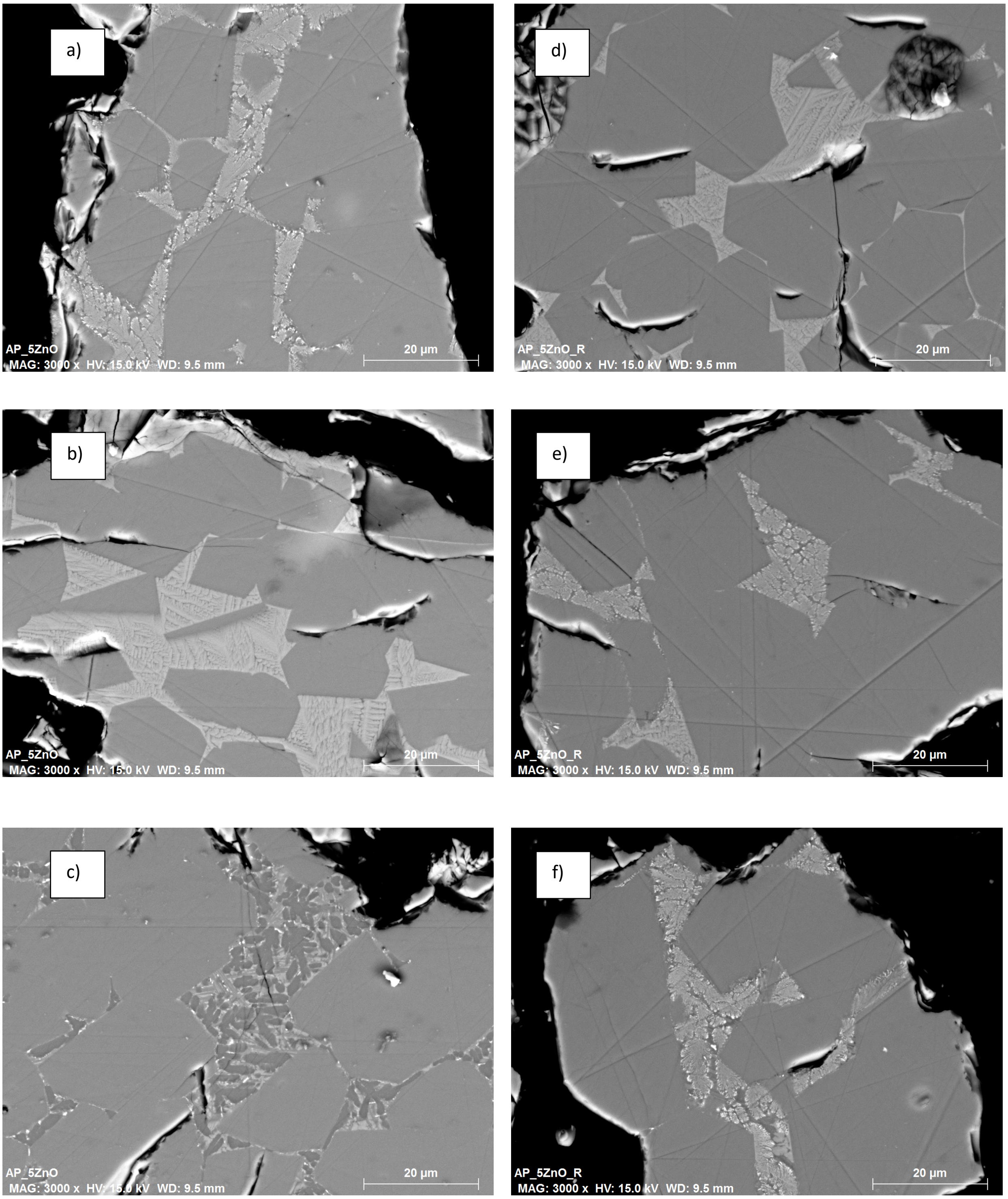

Figure 4-3: Microstructure of the C_3A-Polyclinker 5%ZnO. Without recalcination on the left: a) interstitial A, b) interstitial material with dendritic microstructure, c) interstitial B. Recalcined at 900 °C for 30 min on the right: d) interstitial material with dendritic microstructure, e) and f) interstitial A.

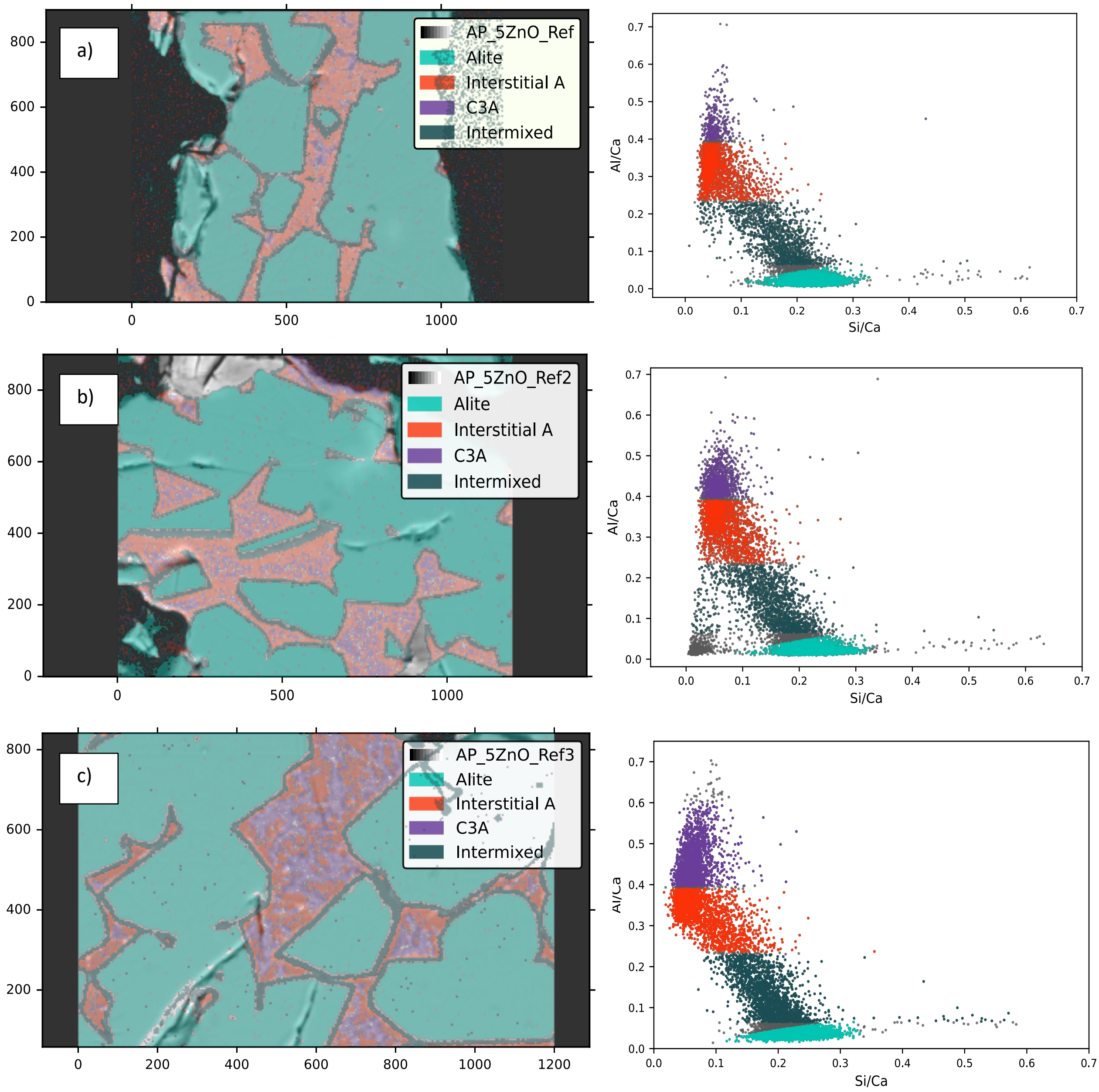

Figure 4-4: Elemental map analysis of the microstructures in figure 4-3, a), b), and c) respectively, of the C_3A-Polyclinker 5%ZnO without thermal treatment. The interstitial material presents different phase distribution.

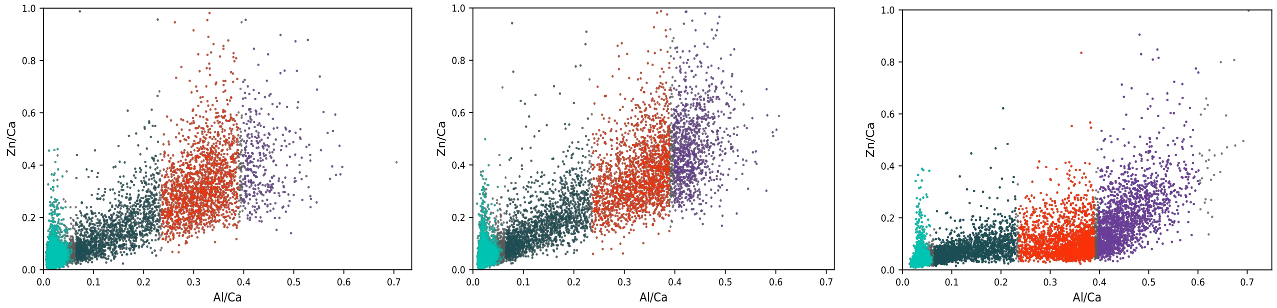

Figure 4-5: Zn repartition of the microstructures in figure 4-3, a), b), and c) respectively, of the C_3A-Polyclinker 5%ZnO without thermal treatment. The concentration of Zn increases with Al.

It was evidenced, with XRD and SEM, that the recalcination process influences the phase composition, interstitial material microstructure, and the same is for the Zn repartition. It was found that more Zn is retained by the alite in the recalcined system (figure 4-6). Thus, with this thermal treatment, a partial recrystallization of the amorphous phase is achieved, which leads to a better ion distribution.

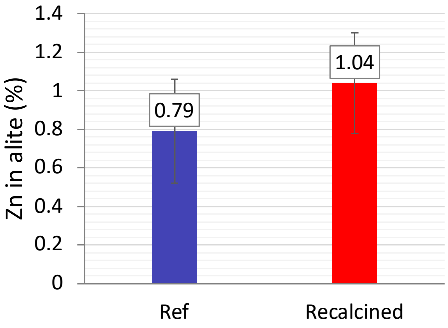

Figure 4-6: Repartition of Zn in alite in C_3A-Polyclinker doped with 5% ZnO, reference, and recalcined.

In terms of reactivity, the annealing affects more the C_3A peak than the alite. It allows recrystallization of the amorphous phase, hence an increase in the reactivity, and confirms that the amorphous phase is indeed related to the C_3A phase (figure 4.7). Beyond that, the amorphous content seems to not be the controlling factor in the length of the induction period. Perhaps, the quality of this amorphous phase, its content of Zn is more important and must be studied. Moreover, similar ZnO content was found for both samples, which can be link with the similar length of the induction period. Additionally, the alite peak is slightly higher in the recalcined sample most probably due to the incorporation of more Zn in alite for this sample.

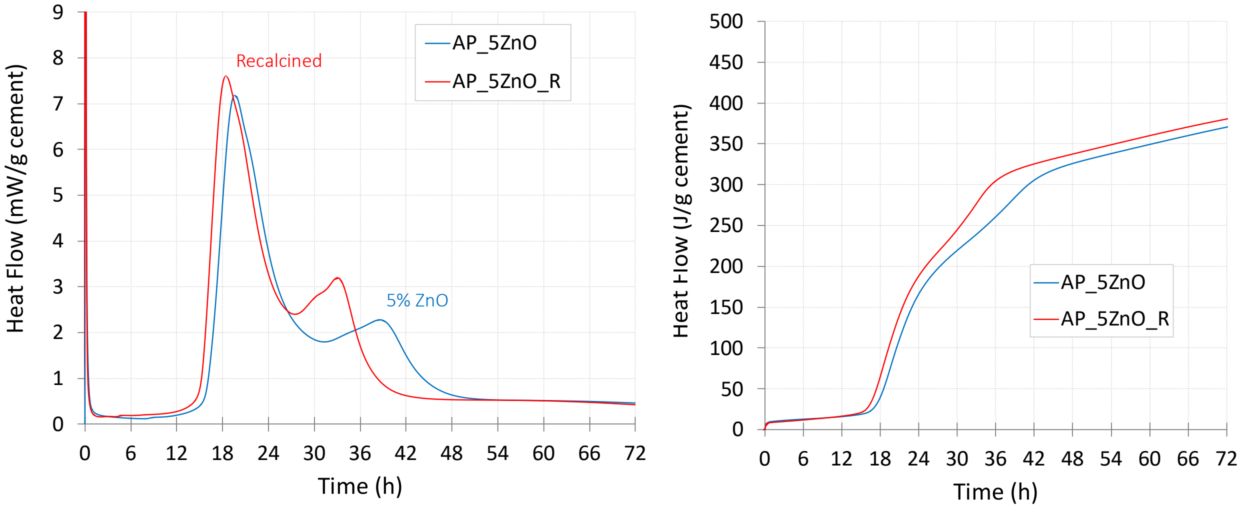

Figure 4-7: Calorimetric curves of C_3A-polyclinker doped with 5% ZnO, recalcined, without thermal treatment, both with 5% of gypsum.

Furthermore, no significant difference in the particle size distribution was observed (figure 4-8), and the specific surface area is very similar (table 4-3).

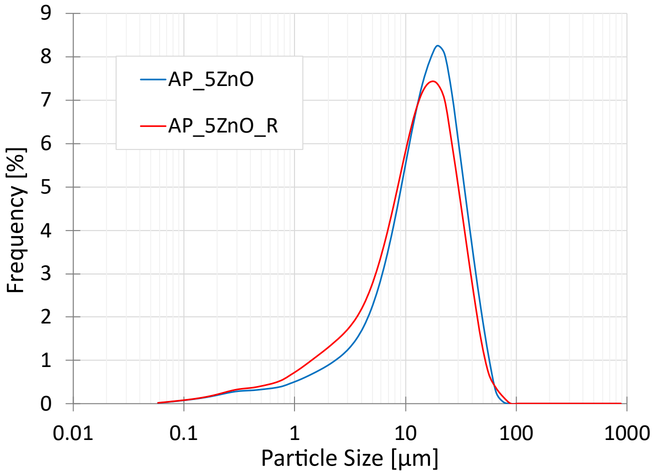

Figure 4-8: Comparison of the particle size distribution of C_3A-polyclinker doped with 5% ZnO, recalcined and without thermal treatment.

Table 4-3: Average particle size (Dv_{50}) and specific surface area (SSA), measured by laser diffraction and nitrogen adsorption respectively, of the C_3A-polyclinker 5% ZnO, recalcined and without thermal treatment.

	Dv50 (µm)	BET SSA (m^2/g)
AP_5ZnO	22.33	0.6020
AP_5ZnO_R	20.80	0.6088

Previous work on thermally treated cement grains showed a reduction in defect density due to a removal of a damaged surface. The most important consequence of this annealing process is on the induction period, which was extended linearly with the temperature and duration of the thermal treatment [11]. To discard this possibility, the same experiment was done with a reference system without ZnO. Again, a new batch of C_3A-Polyclinker was synthesized, this time without doping, and recalcined after the same treatment. Figure 4-9 shows the calorimetric curves of the undoped and the doped system. The samples without ZnO showed similar behavior for the aluminate peak. In this case, the aluminate peak is sharper and occurs earlier for the recalcined sample than for the reference without thermal treatment. The opposite is observed for the alite peak, which is delayed and shorter than for the untreated sample. This effect was not obtained for the polyclinker with 5% ZnO; hence, the extended induction period of these samples, when recalcined, is not caused by the annealing treatment and is more consistent with retardation caused by the free ZnO that remained uncombined in the clinker phases.

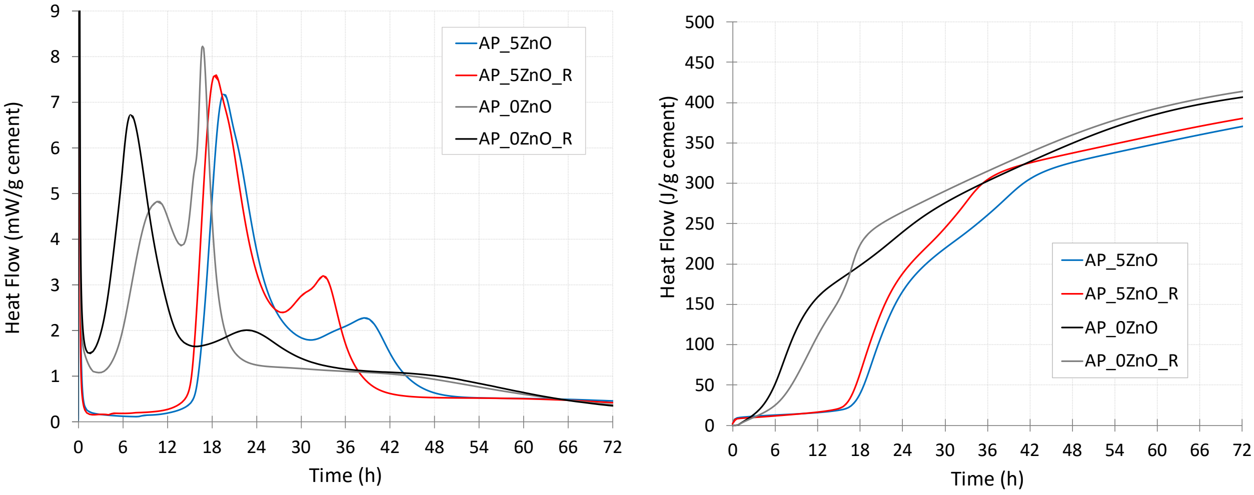

Figure 4-9: Calorimetric curves of C_3A-polyclinker doped with 5% ZnO and undoped reference, recalcined and without thermal treatment, all with 5% gypsum.

The thermal treatment was carried out at 900 °C for 30 minutes, since this is the lowest temperature closest to the crystallization point of the amorphous interstitial material. However, the other extreme, around the melting temperature, is worth investigating since a higher temperature promotes diffusion of ions and is closer to alite formation. Thus, it is probable that more alite, more Zn in the alite and less free ZnO will be obtained, which could potentially shorten the induction period.

4.3.2 C_4AF vs. C_3A polyclinker

As the aluminate phase retains the majority of Zn, a polyphase system with C_4AF is worth investigating as it could allow more Zn to be taken by the alite phase.

Even though the mix design was for a system intended to be 90% alite and 10% C_4AF, after various trials, the closest system, which could be obtained was 80.20% alite, 10.30% C_4AF, 3.13% C_3A, and 6.10% amorphous as shown in table 4-4. The amorphous content increases with ZnO doping. However, the increase in amount is not linear and remains similar between the different dosages of ZnO. The same is observed for the ferrite phase, with content around 12% in all the systems. But compared to the reference system, Zn promotes the formation of C_4AF over C_3A. Zhu et al. concluded that Zn replaces Ca ions in the silicate phases, but the majority of Zn goes to the C_4AF replacing Fe ions which leads to a decrease in the C_3A content [12]. The alite content decreases with the amount of Zn as seen for the C_3A-Polyclinker. Free ZnO was found in the sample doped with 3 and 5% ZnO, and the content increased with Zn dosage.

With slow cooling, the same trend is observed (table 4-5). Less alite is detected in the doped systems, while the amorphous content increases, and in this case, the sample with 1% ZnO has the highest amount of amorphous, showing the non-linearity of Zn doping. Again, Zn does not seem to have an effect on the C_4AF content as similar values were detected.

Table 4-4: Phase quantification of C_4AF-Polyclinker (FP) fast-cooled.

Phase (%) / Sample	**FP**	**FP_1ZnO**	**FP_3ZnO**	**FP_5ZnO**
C_3S (M)	80.20	76.20	76.90	75.50
C_2S	0.26	2.35	0.49	0.16
C_3A	3.13	0.35	0.05	0.58
C_4AF	10.30	11.59	12.27	11.83
CaO	0.00	0.02	0.00	0.09
ZnO	0.00	0.00	0.50	1.32
MgO	0.00	0.00	0.61	0.63
Amorphous	6.10	9.50	9.10	9.90

Table 4-5: Phase quantification of C_4AF-Polyclinker slow cooled.

Phase (%) / Sample	**FP**	**FP_1ZnO**	**FP_3ZnO**	**FP_5ZnO**
C_3S (M)	80.2	78.90	79.00	76.80
C_2S	0.19	0.00	0.00	1.60
C_3A	1.00	0.18	0.10	0.46
C_4AF	12.29	11.72	11.75	11.90
CaO	0.17	0.04	0.00	0.00
ZnO	0.00	0.00	0.48	1.42
MgO	0.00	0.00	0.75	0.59
Amorphous	5.50	9.20	7.90	7.30

Figure 4-10 shows the comparison between the C_4AF-Polyclinker fast and slow cooled. With the slow cooling, the amorphous content decreases, and the difference increases monotonically with Zn, while the C_3S is promoted, as seen for the C_3A-Polyclinker case. However, a slow cooling rate does not have a significant impact compared to the C_3A-Polyclinker system. Moreover, the C_4AF in the reference system is favored over the C_3A with a slow cooling rate. For the doped systems, the C_4AF content does not seem to depend on the cooling rate as it is similar in both cases.

In the C_3A-polyclinker system, as seen in chapter 3, the amorphous content increases with ZnO doping while C_3A decreases. Slow cooling changes this and allows C_3A to crystallize from the melt. Hence, it was proposed that the amorphous phase corresponds to a nanocrystalline or amorphous C_3A that does not have time to crystallize upon cooling. This hypothesis is supported by the results in figure 4-11. The C_4AF content of the Zn doped samples does not depend on the cooling rate as seen for the C_3A polyclinker.

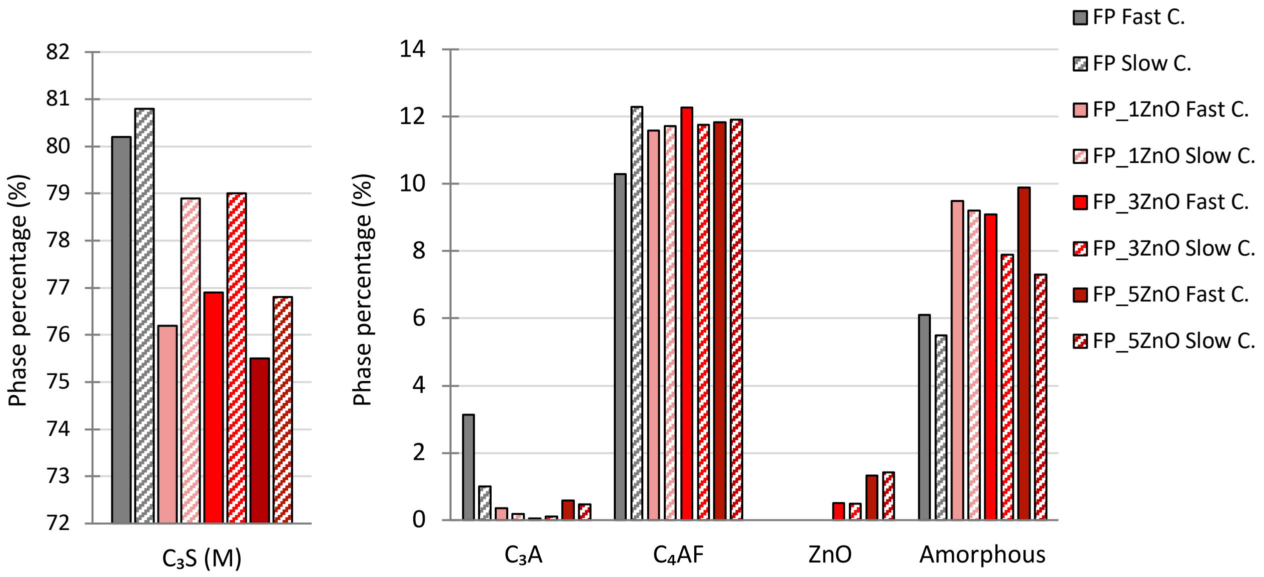

Figure 4-10: Phase comparison of the C_4AF-Polyclinker (FP) system, fast and slow cooled.

In the particle size distribution shown in figure 4-11, the curve shifts slightly to smaller sizes with a slow cooling rate. In table 4-6 the Dv_{50} and specific surface area are indicated and indeed the average particle size is smaller for the slowly cooled samples except for the 3% ZnO system in which the calculated Dv_{50} increases, however, the particle size distribution is very similar for both cooling rates. No fixed trend was found for the SSA although the 3% ZnO system has very similar values independently of the cooling rate.

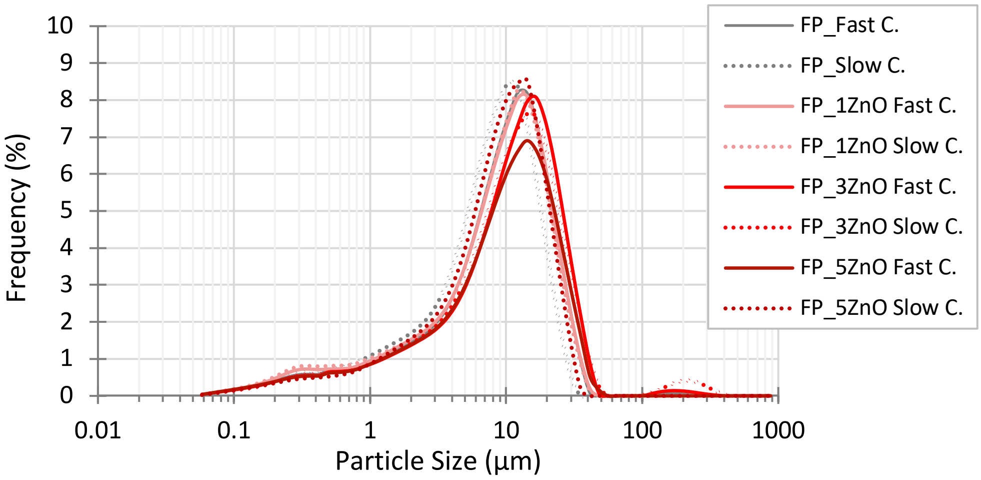

Figure 4-11: Comparison of the particle size distribution of C_4AF-Polyclinker system.

Table 4-6: Average particle size (Dv_{50}) and specific surface area (SSA), measured by laser diffraction and nitrogen adsorption respectively, of the C_4AF-Polyclinker system fast and slow cooled.

	Dv_{50} (µm)	**BET SSA (m^2/g)**
FP Fast C.	14.83	0.6670
FP Slow C.	11.54	0.5889
FP_1ZnO Fast C.	14.47	0.6689
FP_1ZnO Slow C.	14.07	0.9360
FP_3ZnO Fast C.	18.27	0.6304
FP_3ZnO Slow C.	21.81	0.6495
FP_5ZnO Fast C.	16.08	0.8545
FP_5ZnO Slow C.	13.24	0.9163

The microstructures of this system are shown in figure 4-12. The reference systems, both fast and slow cooled, have a brighter interstitial material compared with the reference system of the C_3A-Polyclinker. This is because there is C_4AF instead of C_3A in this case and the presence of iron backscatters more electrons which results in a brighter phase in a grey level contrast. Moreover, white spots can be observed in the samples with 3 and 5% ZnO, regardless of the cooling rate, and they are more abundant in the sample with 5% ZnO. The microstructure of the polyclinker with 1% ZnO is comparable with the reference system as no white spots can be seen. However, with 1% ZnO more interstitial materials form, meaning that ZnO indeed promotes more liquid phase during the clinkerisation process that is then partially recrystallized as an interstitial material. All these observations match the XRD results in figure 4-10.

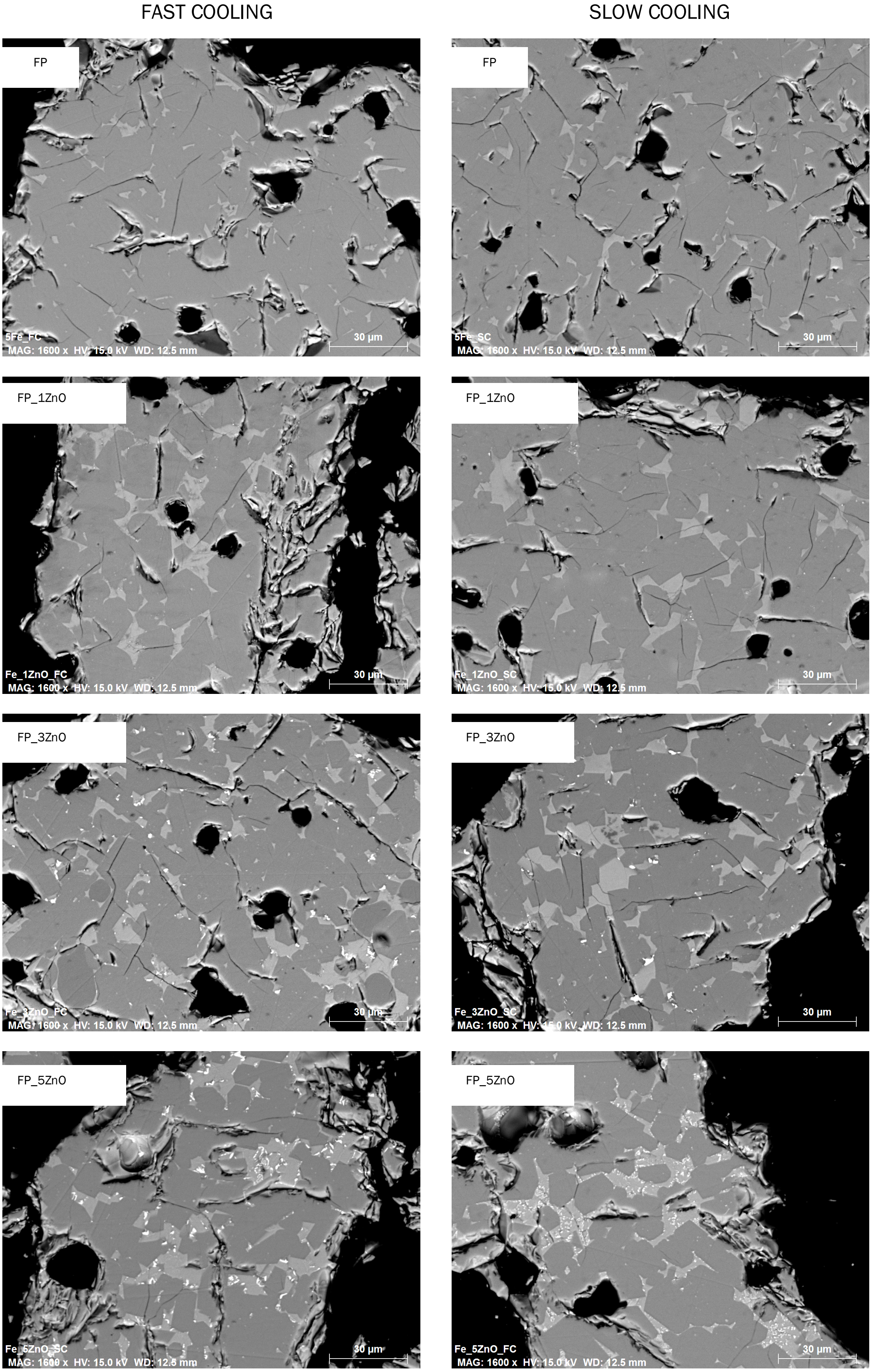

Figure 4-12: Microstructure comparison between C_4AF-Polyclinker system (FP), fast and slow cooled.

More ZnO remains uncombined with the amount of ZnO in the raw materials, and this seems not to depend on the cooling rate for the C_4AF-Polyclinker. Furthermore, figure 4-13 shows the estimated amount of Zn retained by alite and the same trend seen for the C_3A polyclinker in the previous chapter. The more ZnO in the raw materials, the more Zn will be retained by alite. The error in these values is caused by the interaction volume characteristic of the SEM technique. The size of the error bars increases with the amount of Zn in the system. The interaction volume causes this increase; as more Zn is in the sample, more Zn is in the other clinker phases and uncombined. Hence, the point analysis takes the information of the surroundings.

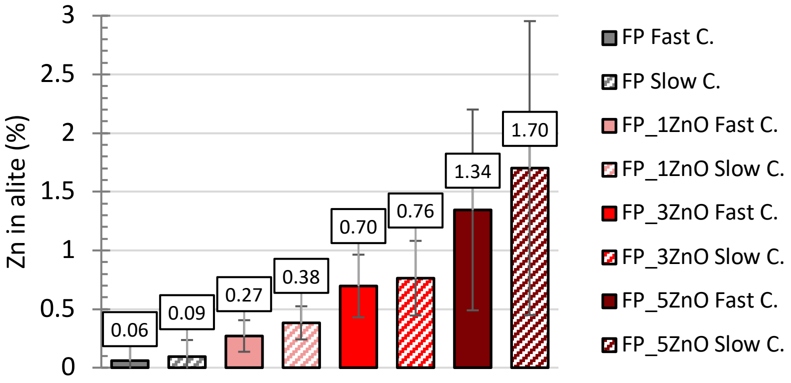

Figure 4-13: The estimated amount of Zn in alite by SEM-EDX point analysis on alite grains of the C_4AF-Polyclinker system (FP) system.

Compared to the values of the C_3A-Polyclinker, more Zn is retained by alite with C_4AF in the case of 5% ZnO (figure 4-14) and even more with a slow cooling rate. Coupling these results with the XRD quantification, as the amorphous content decreases with a slow cooling rate, the Zn in this phase can go to alite, combine with the C_3A to form C_4AF as Zhu et al. [13] proposed, and partly remain uncombined. With lower ZnO dosages, no significant difference is found between the two systems. This means that the amount of Zn retained by alite, at low dosages, might not depend on the interstitial material composition. Nevertheless, it depends on the ZnO dosage in the raw materials and the cooling rate at the end of the synthesis process.

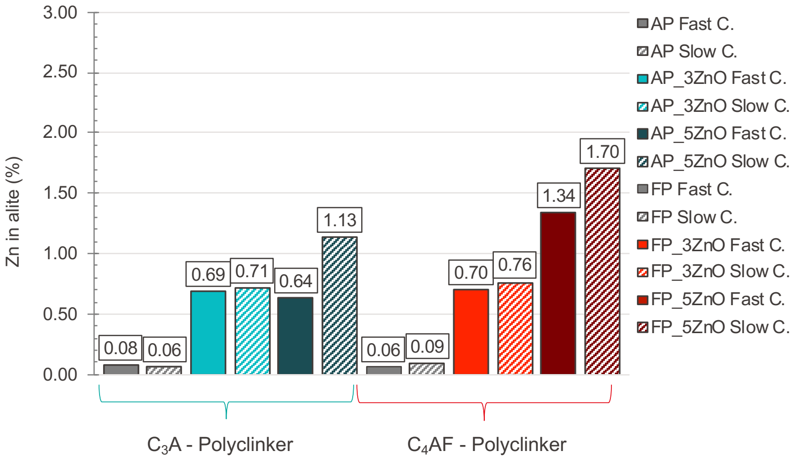

Figure 4-14:Comparison between 10%C_3A-polyclinker (AP) and 10%C_4AF-polyclinker (FP) systems of the estimated amount of Zn in alite by SEM-EDX point analysis on alite grains.

The calorimetric curve of the 3% ZnO sample with and without gypsum is shown in figure 4-15, and it is also compared with the reference system to which 5% gypsum was added. The samples were mixed with a w/c = 0.5. As seen, the addition of gypsum to the doped sample causes severe retardation; the alite peak appears after 216 hours. Even though the reference system exhibits a properly sulfated behavior with 5% of gypsum addition, it was decided to study the hydration of the FP systems doped with ZnO without the addition of gypsum, considering that it is added to control C_3A reaction, which and that the FP system is mainly C_4AF. However, the interaction between sulfates and Zinc is worth investigating, as reported in chapter 5.

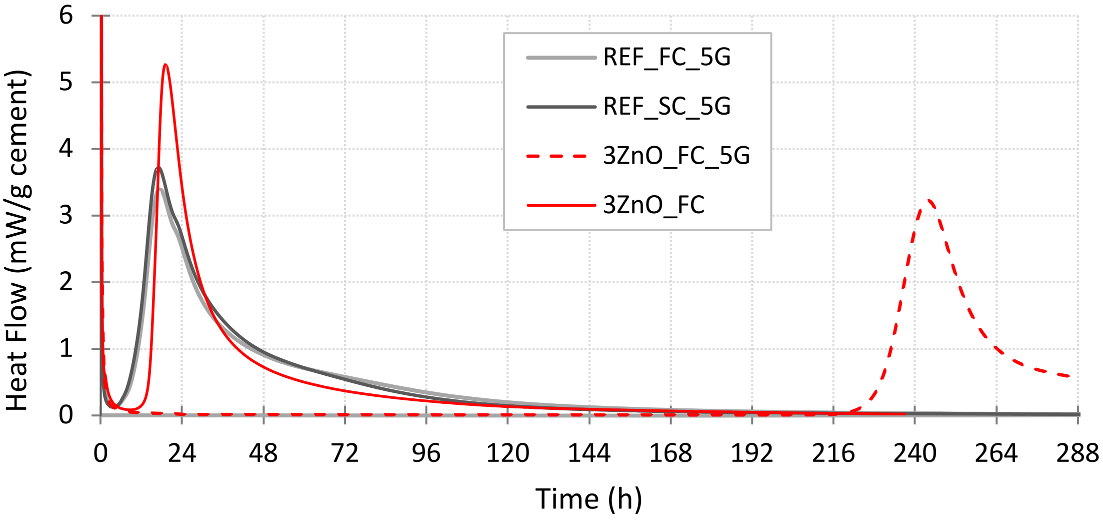

Figure 4-15: Calorimetric curves FP reference system with 5% gypsum and fp 3%ZnO with 5% gypsum and without.

Figure 4-16 shows the calorimetric curves of the FP system. The shape of the curves looks like the alite system in chapter 3 as only the silicate peak is seen. The retardation of the doped system in relation to the reference can come from the “free ZnO” that remains uncombined, as seen by other researchers before. However, higher heat released was registered in the doped samples, and the height of the peak increases with Zn dosage when fast cooled. This follows the initial hypothesis of: Zn in the alite phase increases the reactivity by the incorporation of Zn in the C-S-H, as more Zn is found in alite (figure 4-13).

There is no linear or monotonic behavior with the Zn dosage. The alite peak of the samples with 3 and 5% ZnO appears before the sample with 1% ZnO. If the curves from the slowly cooled samples are compared, there is no clear trend either. However, between the FP 3ZnO and 5ZnO similarities are found. The alite peak of the slow cooled samples happens after the fast cooled ones. Which is the opposite of what was observed for the C_3A-Polyclinker. This can be explained in terms of free ZnO again. Additionally, the height of the peak for these two systems is lower compared to the fast cooled samples. As Zn increases the reactivity of alite by being incorporated in the C-S-H, perhaps what happened here is that less C-S-H was formed due to the lack of space produced by the calcium zincate. And this seems to match for every sample as the height of the peak is lower for a longer induction period. Even for the sample with 1% ZnO which has an opposite behavior with respect to the cooling rate. No free ZnO was detected in this system, neither with XRD nor with SEM. Hence, its behavior can be related to the amorphous content which stays similar for both cooling rates and might contain enough Zn to retard the hydration at a slower dissolution rate compared to free ZnO. Nevertheless, this hypothesis must be further studied.

To sum up this 4.3 section, in a C_4AF-polyclinker doped with ZnO, more Zn was found in alite and more free ZnO as the dosage increased. In terms of reactivity, the alite peak height is increased with more Zn in alite which supports the hypothesis previously exposed. However, longer induction period was observed and related to the free ZnO detected with XRD and SEM. Slow cooling rate does not seem to enhance the reactivity of these systems compared with the C_3A-Polyclinker. Moreover, severe retardation was found when added gypsum to the doped samples. This effect will be further discussed in chapter 5.

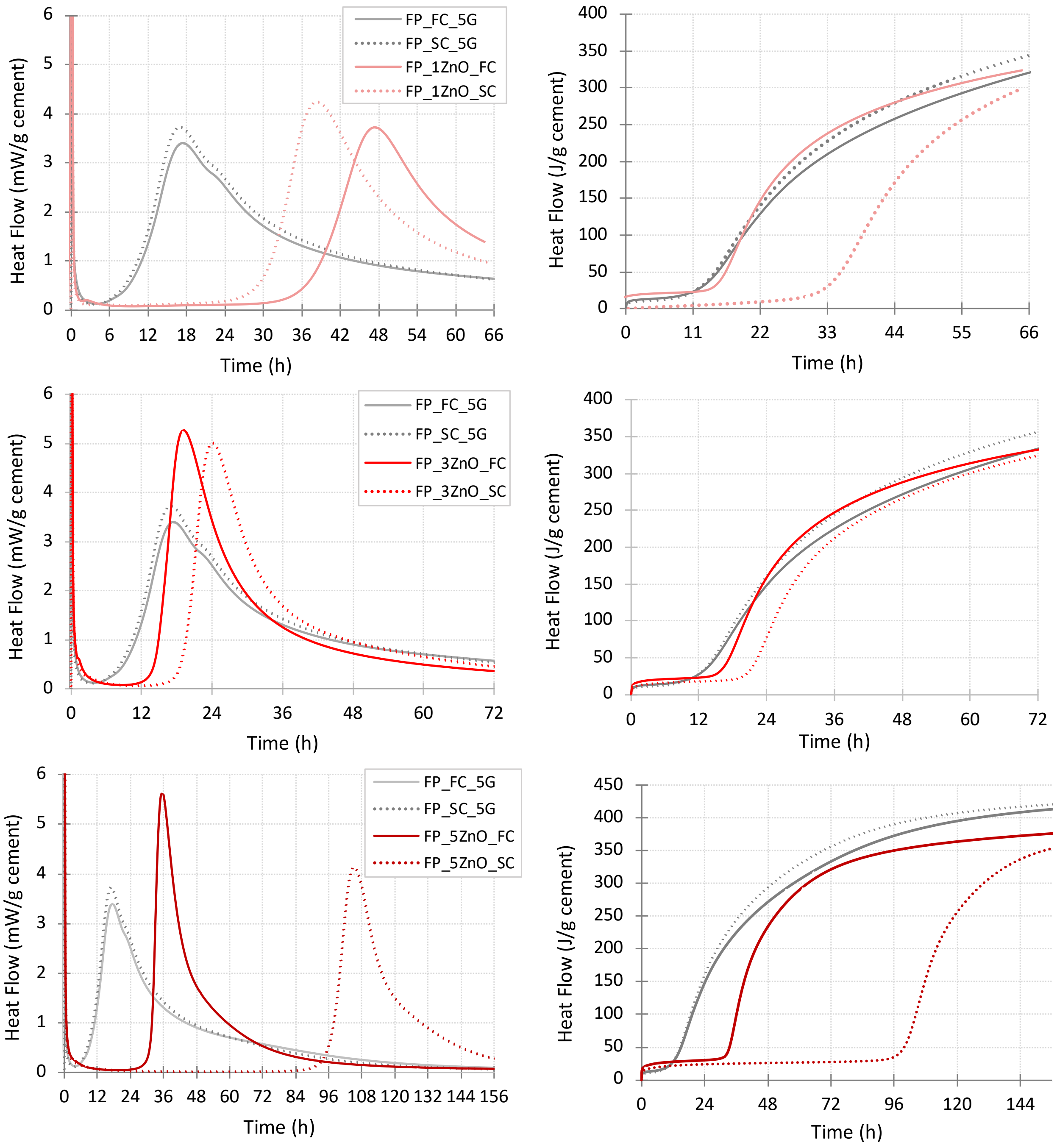

Figure 4-16: Calorimetric curves of the 10%C_4AF polyclinker system (FP). 5% of gypsum was added to the reference samples. Doped samples without gypsum.

4.3.3 10% vs 5% C_4AF polyclinker

The other approach is to decrease the amount of interstitial material from 10% to 5%. As Zn likes to be in this phase, reducing its amount could allow more Zn to be retained by alite or, on the contrary, more concentration of Zn in the interstitial material or remain uncombined as free ZnO.

The XRD quantification shows the same trend as seen before (table 4-7), and figure 4-17 shows a visual comparison of these results. A lab-scale polyclinker with a high alite content (90%) was produced with only 5% of C_4AF at 1450 °C. Moreover, the ZnO doping increased the amorphous content while decreasing the C_3S one, as noticed before. In this case, the C_4AF content was raised with the ZnO doping. This can be related to the substitution of Fe ions by Zn ones proposed by Zhu et al. [13]. With a slow cooling, more C_3S and less amorphous are formed; however, it is not as significant as for the C_3A-polyclinker system. For the reference sample, more C_4AF was promoted with slow cooling, and the same was observed for the doped sample.

Table 4-7: Phase quantification of 5%C_4AF polyclinker system.

Phase (%) / Sample	**REFERENCE**		**3%ZnO**	
	Fast C.	**Slow C.**	**Fast C.**	**Slow C.**
C_3S (M)	88.40	90.00	80.80	82.10
C_2S	0.00	0.00	0.00	0.26
C_3A	1.48	0.00	0.00	0.00
C_4AF	2.77	4.03	4.78	5.01
CaO	0.00	0.00	1.53	1.55
ZnO	0.00	0.00	0.25	0.22
Amorphous	7.30	6.00	12.70	10.80

It is curious that with a lower quantity of iron in the raw materials and with a mix design intended to have less interstitial material, the amorphous content is higher than for the C_4AF-polyclinker system intended to have 10% C_4AF (figure 4-18) for both, reference and 3% ZnO doped system. Hence, the amorphous content not only depends on the composition of the liquid phase formed during synthesis, but on Zn doping, that clearly has an impact on increasing its amount.

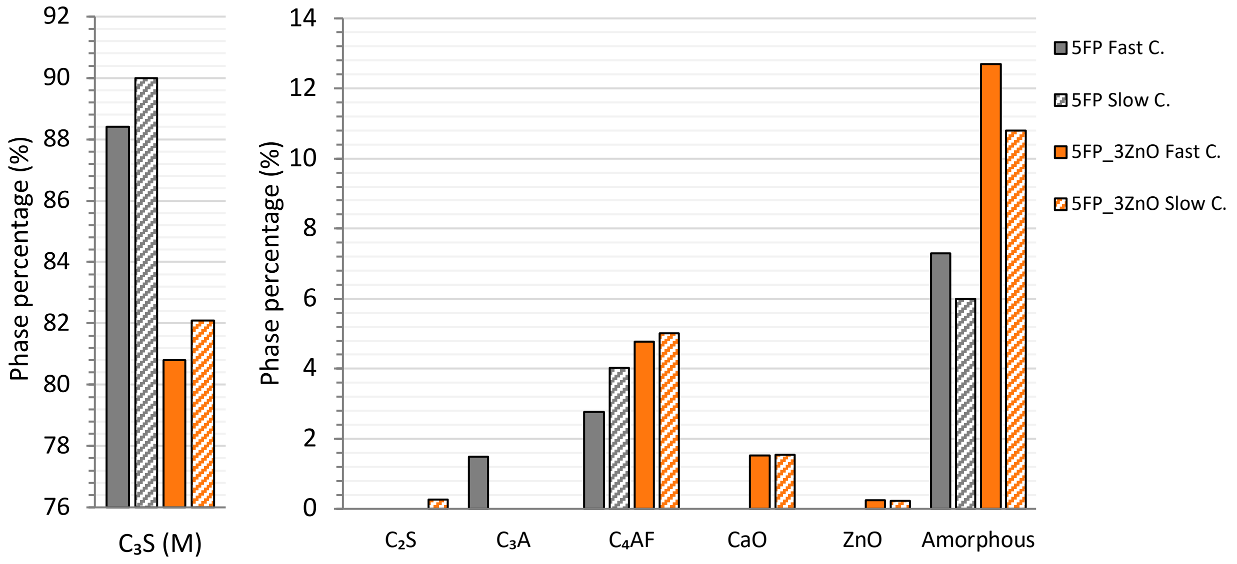

Figure 4-17: Phase quantification between 5%C_4AF polyclinker system (5FP), fast and slow cooled, and doped with 3% ZnO.

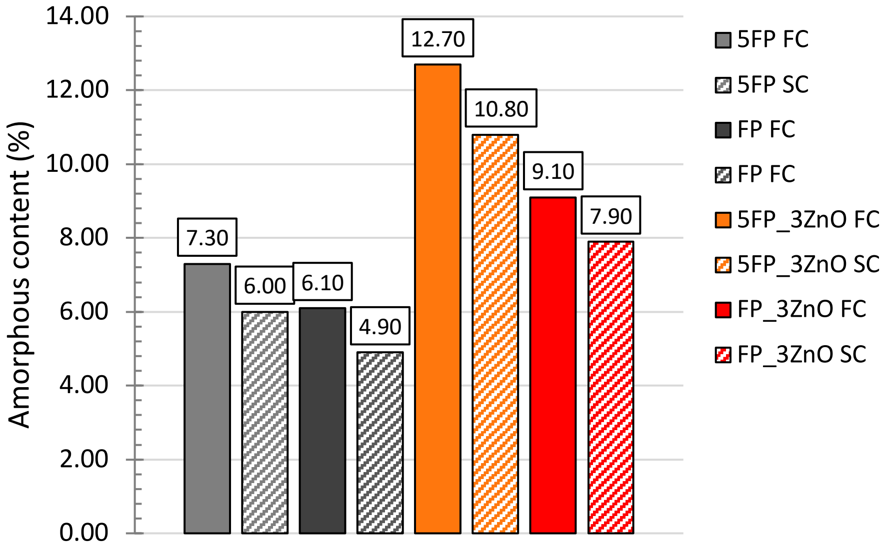

Figure 4-18: Comparison of amorphous content between the 5% C_4AF (5FP) and 10% C_4AF (FP)-polyclinker systems, reference and doped with 3%ZnO (FC = fast cooling, SC = slow cooling).

With the particle size distribution in figure 4-19 it is difficult to find a trend. For the reference, the curve is shifted to the left and hence bigger particle size was found for the slowly cooled sample compared to the fast cooled. The doped sample shows the opposite, with a slow cooling smaller particles were found (table 4-8). Therefore, there is not a clear trend nor with the cooling rate nor the doping as seen previously for the 10% C_4AF polyclinker.

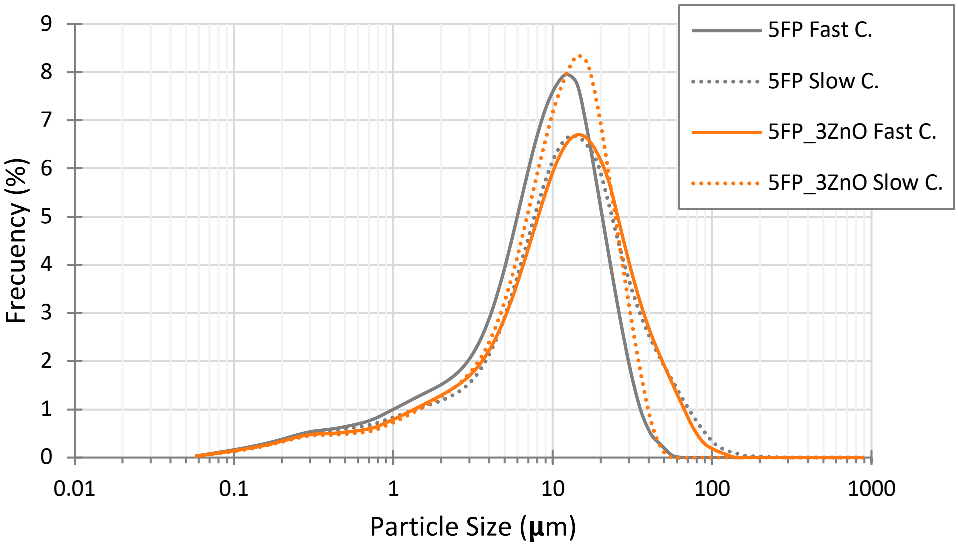

Figure 4-19: Comparison of the particle size distribution of 5% C_4AF-polyclinker system (5FP).

Table 4-8: Phase quantification of 5%C_4AF polyclinker system (5FP).

	Dv_{50} (µm)	**BET SSA (m^2/g)**
5FP Fast C.	14.02	0.7557
5FP Slow C.	24.23	0.7250
5FP_3ZnO Fast C.	22.98	0.7707
5FP_3ZnO Slow C.	16.04	0.7043

The microstructures in figure 4-20 are like those of 10% C_4AF-polyclinker system. In the doped system, more interstitial material can be observed and white spots as well. These white spots correspond to the free ZnO that remains uncombined as seen for the 10% C_4AF-polyclinker system. The cooling rate does not seem to have an effect in the microstructure.

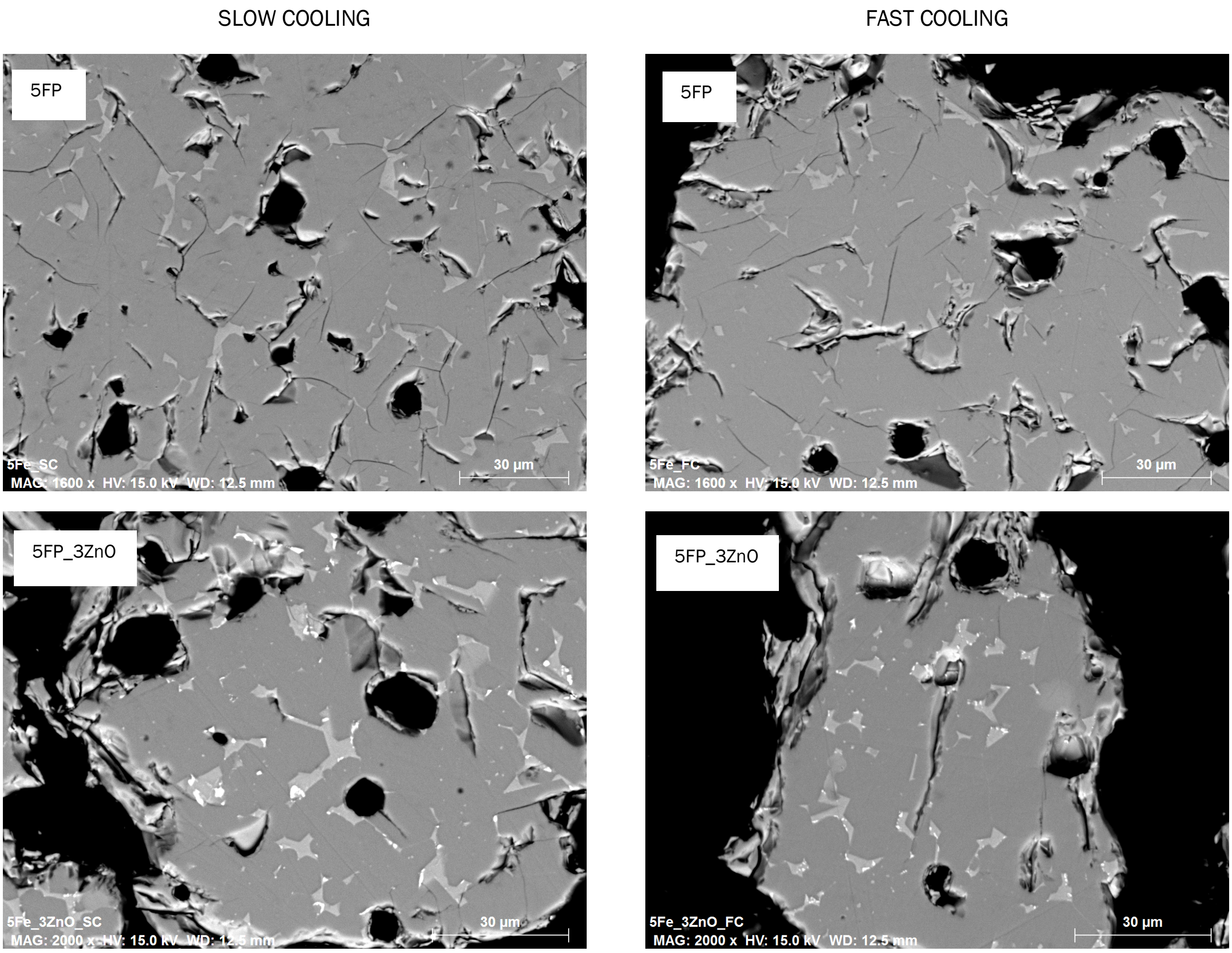

Figure 4-20: Microstructure comparison between 5%C_4AF-polyclinker system (5FP), fast and slow cooled.

Less free ZnO was found in the polyclinker with 5% C_4AF compared to the 10% C_4AF (figure 4-21), and it slightly decreases with a slow cooling rate. Hence, where is the Zn going? Is it being retained by the alite or in the amorphous phase? The SEM-EDX point analysis showed that more Zn is in alite when the ferrite phase is decreased to 5%, and slightly more can be promoted with a slow cooling rate (figure 4-21).

The calorimetric curves in figure 4-22 correspond to the 5%C_4AF-polyclinker system in where 5% of gypsum was added only to the reference samples. The doped ones were mixed directly with water with a w/c = 0.5. Eventhough the presence of Zn causes retardation, the height of the peak is increased, and it is narrower, similarly to what it was seen for the 10% C_4AF system (figure 4-16). And again, the slow cooled sample is more retarded. The cumulative heat showed that even when the peak is higher, the total heat released is lower.

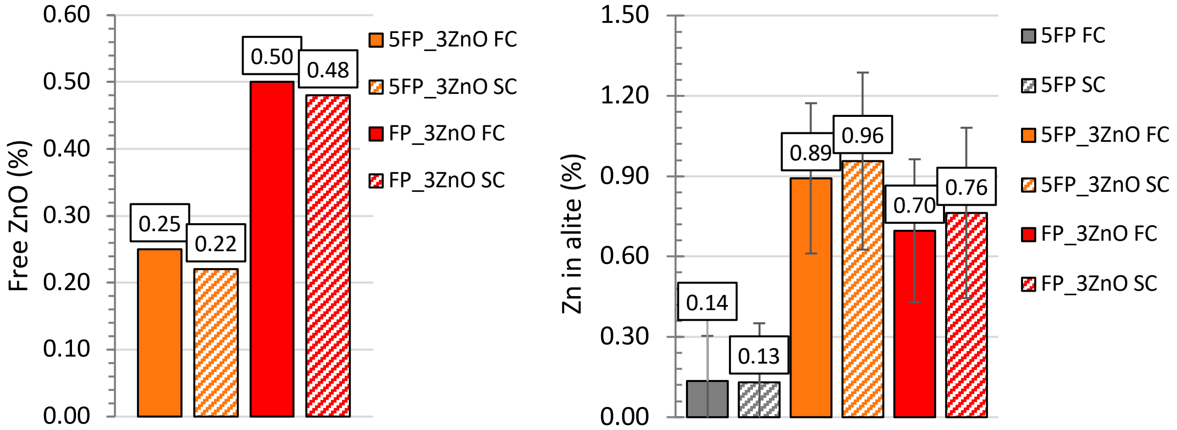

Figure 4-21: Comparison between the 5%C_4AF and 10%C_4AF polyclinker systems (5FP and FP) of: the free ZnO in samples doped with 3%ZnO (right); the Zn in alite from the reference and doped with 3% ZnO, with a fast and slow cooling rate (left).

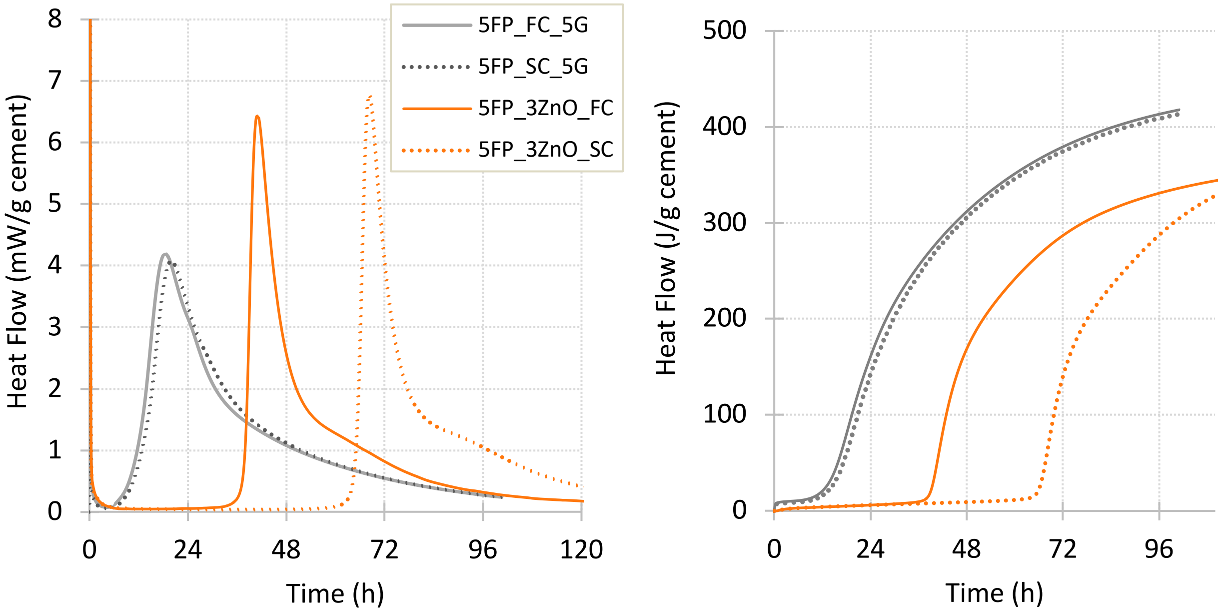

Figure 4-22: Calorimetric curves of the 5%C_4AF polyclinker system (5FP). 5% of gypsum was added to the reference samples. Doped samples without gypsum.

The induction period is longer compared to the 10% C_4AF polyclinker doped with 3% ZnO (compared to figure 4-16). For the 5% C_4AF system, the induction period ends around 36 hours while for the 10% C_4AF system it happens at around 12 hours. This retardation could be attributed to the amount of amorphous, being higher for the 5% C_4AF. Yet, when more alite is formed, and then more Zn is in alite compared to other systems, the amorphous content and free ZnO seem to be more critical factors.

4.4 Conclusions

Three different approaches were studied as possibilities to retain more Zn in alite. A higher tendency of Zn in alite was found in all of them.

- Recalcination of the C_3A-polyclinker:

A thermal treatment of 900 °C for 30 min in a C_3A-Polyclinker doped with 5% ZnO decreased the amount of amorphous, and more Zn was detected in alite. It has a higher impact on the C_3A hydration, which resulted to be faster due to the recrystallization. The induction period was slightly decreased but still longer than the reference without doping. Hence, the retardation was related to the free ZnO, which was similar in both samples.

- Effect of C_4AF as the interstitial material:

  More Zn was retained by alite, but also more free ZnO was found which is responsible for the retardation observed. However, the alite peak was increased with ZnO dosage. The retardation in the sample with 1% ZnO was related to the amount of amorphous as no ZnO was detected.

- Lower amount of interstitial material:

  Even when more Zn was found in alite, extended induction period was seen compared to the 10% C_4AF system and again related to the amorphous content. Furthermore, a high alite content polyclinker was synthesized at 1450 °C with only 5% C_4AF.

Even when more Zn can be retained by alite, the amorphous and free ZnO are more dominant in terms of hydration kinetics leading to longer induction periods.

Severe retardation was found when added gypsum to the doped samples. This effect will be further discussed in chapter 5.

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Chapter 5 Interaction between sulfate and zinc in alite hydration

Note: this chapter is based on an article in preparation for submission to a peer-reviewed journal.

Contribution of the doctoral candidate: writing of the first manuscript draft, experimental design, conduction of experiments and analysis.

Abstract

Minor amounts of ZnO in the raw materials for alite synthesis increase its reactivity, and this was related to an increase in the size of the C-S-H needle length. The addition of calcium sulfate dihydrate, gypsum, causes a similar effect in hydration, also associated with a change in the growth of the C-S-H. Little research has been done on the effect of gypsum on Zn-doped systems. Hence, the aim of this work is to investigate this effect in a Zn-doped alite to enhance hydration. However, the calorimetric curves revealed an extension of the induction period in the presence of sulfates. A high concentration of Zn was found at the start of this period, most probably coming from the fast dissolution of a secondary Zn phase formed during the calcination. It was proposed that an amorphous Zn compound could be the cause of the retardation based on the XRD and SEM analysis

Contents

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5.1 Introduction

Nowadays, the main goal of the cement industry is to find alternatives to replace clinker with more environmentally friendly materials as it is responsible for up to 8% of anthropogenic CO_2 emissions. Minor amounts of Zn in C_3S and alite enhance their reactivity. Hence, it represents a potential solution allowing more clinker replacement by supplementary cementitious materials (SCMs). This enhancement has been related to an increase in the needle length of the C-S-H when Zn is in the alite [1]. However, this effect is not seen in Portland cement, where the Zn is mainly concentrated in the interstitial material rather than in the alite. Depending on the dosage, it can remain uncombined as free ZnO. Severe retardation occurs when ZnO is present. Researchers have found the formation of calcium zincate hydrate to cause this retardation. Zinc ions are rapidly released into the solution and consume calcium to form the calcium zincate [2]–[5].

Calcium sulfate dihydrate or gypsum is added to Portland cement to control the C_3A reaction. It slows down the hydration of the aluminates and consequently increases the workability of cement. Gypsum affects not only the C_3A reaction but also the C_3S, as seen by Zunino and Scrivener [6]. The hydration of C_3S is enhanced in the presence of sulfate, which was associated with a change in the growth of the C-S-H; longer needles were observed during the first 24 hours [7]. Additionally, proper sulfation is important for the performance of blended cements [8]. As C_3S influences this sulfate balance, and Zn in alite represents a potential solution to decrease the clinker factor in blended cement, it is essential to understand the effect of gypsum in Zn-doped alite.

Little research has been done on the effect of gypsum on the hydration of cement containing Zn. Arliguie et al. [9] defended on many occasions the hypothesis that a layer of $Zn(OH)_2$ covers the C_3S grains, retarding its hydration. Additionally, they investigated the impact of different amounts of gypsum on the hydration of cement with 5% Zn (added externally). They concluded that 2.5% or less of sulfate is positive for avoiding the retardation of Zn. They explained that the C_3A reacts faster and continues to bring Ca^{2+} and OH^- ions to the solution that allows the $Zn(OH)_2$ to transform to calcium zincate and the hydration is then renewed. With more than 2.5% of sulfate, the C_3A hydration is retarded, and therefore the C_3S hydration as well by the amorphous $Zn(OH)_2$ layer. They stated that fine ettringite is formed that covers the grains forming a heterogeneous layer together with a zinc hydroxide inhibiting the ionic exchange. Therefore, it takes longer to transform into calcium zincate and the hydration is renewed. However, no evidence of such a layer was given and no interaction between sulfates and zinc was studied. Their research was mainly related to the C_3A reaction and hence the ettringite formation.

Nevertheless, no investigation has been done into the effect of Zn-doped C_3S or alite hydration. This study aims to investigate the impact of gypsum in Zn-doped alite as first attempt to understand the effect in more realistic systems. An alite system was synthesized, undoped and doped with 3% ZnO. The hydration behavior was studied by isothermal calorimetry and the pore solution was analyzed during the induction period and compared to a system with 5% of gypsum.

5.2 Materials and Methods

5.2.1 Raw materials, mix design and synthesis process

The alite and C_3S systems were synthesized following the method developed by Li et al. The raw materials were mixed, following the mix composition in table 5-1, in a zirconia mill jar with water (distilled) for 24 hours. The mix was cast into cylinder molds and slowly dried at 60 °C for 24 hours ad then 110 °C for another day to ensure no more water was in the mix. After drying, the cylinders were demolded and placed into platinum crucibles. The calcination was done at 1600 °C for 3 hours with a heating rate of 7 °C/min in an 1800 °C Borel Swiss furnace. Finally, the material obtained was ground in a disc mill, 100 g for 60 s.

The calcium carbonate is from VWR, the SiO_2 silica fumed from Sigma-Aldrich with a particle size Dv_{50} of 0.007 μm, the aluminum, magnesium, and zinc oxide from MERK, and the iron oxide (99.999%) from Acros Organics.

Table 5-1: Mix composition for alite (A), alite doped with 3% ZnO (A_3), C_3S (C) and C_3S doped with 3% ZnO (C_3). Alite composition was based on the alite composition in the cement chemistry book from H.F.W. Taylor [10].

Raw materials (%) / Sample	**A**	**A_3**	**C**	**C_3**
CaO	70.55	68.43	72.46	70.28
SiO_2	26.82	26.02	27.54	26.72
Al_2O_3	0.74	0.72	0.00	0.00
MgO	1.17	1.13	0.00	0.00
Fe_2O_3	0.73	0.71	0.00	0.00
ZnO	0.00	3.00	0.00	3.00

5.2.2 Experimental methods

X-ray diffraction (XRD) was used to determine the phase composition of the samples, mainly to identify the presence of free lime or free ZnO after the synthesis. The measurements were done in a X'Pert MPD PRO diffractometer with CuKa radiation at 45 kV and 40 mA. The diffractograms were collected from 5 to 70 2θ.

The particle size distribution (PSD) was measured by laser diffraction with a Malvern MasterSizer S with the SHE_3 optical model (n=1.7, k=0.1, n=1.39). The specific surface area was determined by Brunauer–Emmett–Teller 5 points method (SSA-BET), where the nitrogen adsorption-desorption was obtained with a Tristar II plus from Micromeritics.

Isothermal calorimetry at 20°C was used to evaluate the reactivity of the samples. First, the powder samples were mixed with water to a solid ratio of 0.5 for 2 min with a speed of 1600 rpm with an IKA eutostar 40 mixer. Second, 10g of paste was placed into glass ampoules which were then closed. Then the ampoules were placed inside the corresponding calorimeter channel. The data were acquired during two weeks. 5% of gypsum, calcium sulfate dihydrate from ROTH, 98% was added.

For the pore solution analysis, the pastes were prepared with 20 g of sample with a w/c = 0.5, mixed with destilled water as for calorimetry, and then placed into conical tubes of 50 ml. The pore solution was extracted by centrifugation with a Hermle Z 206 A rotor at 6000 rpm with an acceleration of 5 steps for 5 minutes. After, the solution was collected with a syringe and filtered with a micro filter of 0.2 μm. An automatic pipet was used to take 1.5 ml of solution and diluted three times with nitric acid 1%. The samples were kept under refrigeration conditions until the measurement by the central environmental laboratory at EPFL. Calcium and silicon were measured by inductively coupled plasma optical emission spectrometry (ICP-OES: Shimadzu ICPE-9000); aluminum and zinc by ICP-mass spectrometry (ICP-MS: Agilent Technologies LC Infinity II ICP-MS Triple Quad 8900); and SO_4^{2-} by ion chromatography (IC: Thermo Scientific Intergrion HPIC). The pH was measure by a pH electrode (BlueLine 14 pH, SI Analytics).

Scanning electron microscopy (SEM) coupled with energy dispersive X-ray (SEM-EDX) was used to analyze the microstructure of the alite. The powder was impregnated in resin, polished, and coated with carbon. The equipment used was a FEI Quanta 200 microscope with a back-scattered electrons (BSE) mode and operating at 15 kV. The morphology evolution was studied by scanning electron microscopy (SEM). For secondary electrons (SEM-SE), the dried samples were crushed, spread on a conductive tape, and then coated with 7nm of Iridium. In this case, a Zeiss Merlin microscope was used. The samples were dried by isopropanol filtration.

5.3 Results and discussion

5.3.1 Characterization of the synthesized alite and C_3S doped with ZnO

The quality of the samples can be studied in terms of free CaO and/or free ZnO given by XRD. Table 5-2 shows the phase composition of both systems. No free ZnO was found in the samples by Rietveld quantification. However, if the diffractograms of the alite system are compared (figure 5-1), the characteristic peaks of the zincite at 31 and 37 can be seen. Hence, alite doped with 3% ZnO may contain minor amounts of this phase.

Table 5-2: Phase quantification of alite (A) and C_3S (C), reference and doped with 3% ZnO (A_3 and C_3).

Phase (%) / sample	**A**	**A_3**	**C**	**C_3**
C_3S	99.6	98.2	98.5	98.1
C_2S	0.0	0.0	1.2	1.4
CaO	0.4	1.7	0.3	1.5
ZnO	0.0	0.0	0.0	0.0

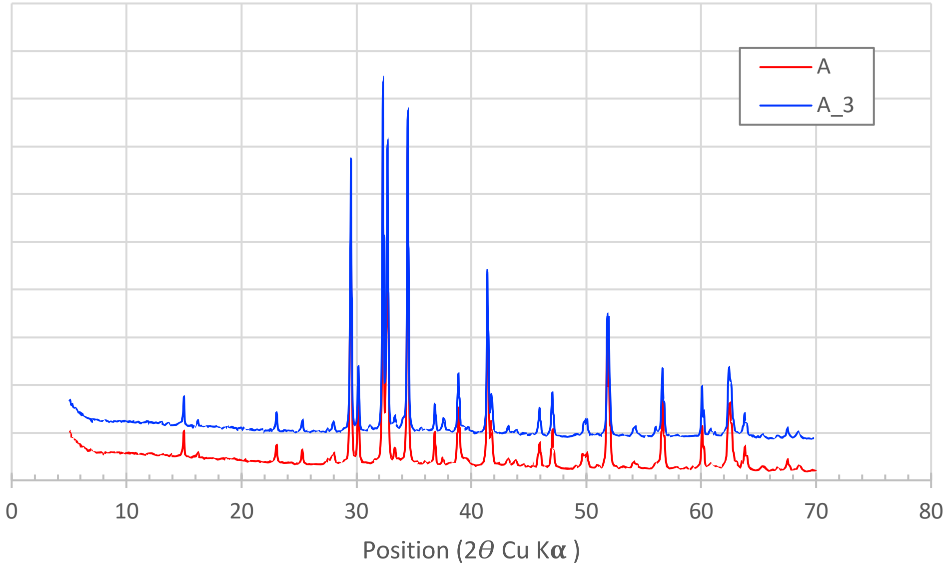

Figure 5-1: Diffractograms of the alite (A) system showing ZnO peaks in the doped sample (A_3).

The particle size distribution is different between the systems. The PSD of the alite system is unimodal while bimodal distribution was found for the C_3S system, and this is towards a smaller particle size (figure 5-2).

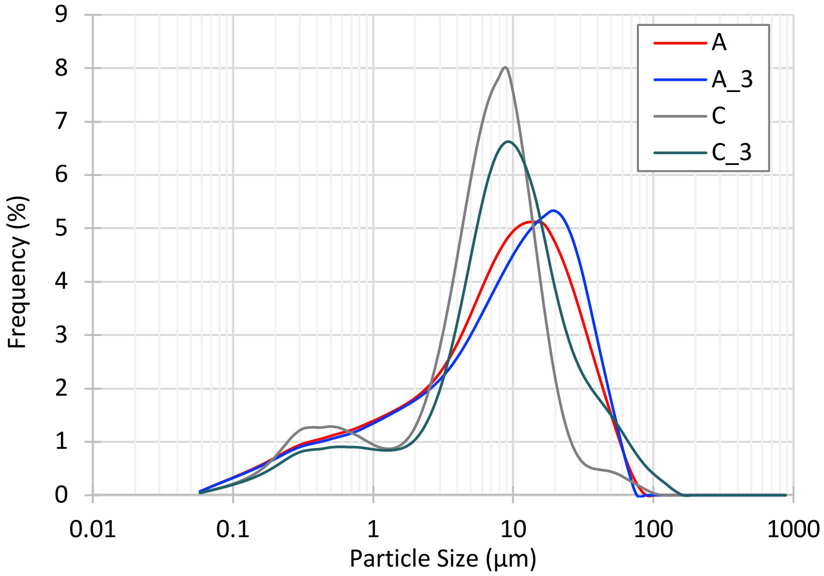

Figure 5-2: The particle size distribution of the C_3S (C) and alite (A) systems, bimodal and unimodal respectively.

Table 5-3 shows a smaller Dv_{50} for the C_3S compared to the alite system, with a tendency for an increase in particle size when they are doped with ZnO. Besides, the specific surface area decreases with Zn doping, and the C_3S system was found to be rougher than the alite.

Table 5-3: The average particle size (Dv_{50}) and the specific surface area (SSA) of the C_3S (C) and alite (A) systems.

	Dv_{50} (µm)	**BET SSA (m^2/g)**
A	21.31	1.1705
A_3	22.83	1.0886
C	11.25	1.8663
C_3	20.97	1.3059

5.3.2 Effect of gypsum in Zn doped alite

The hydration of alite is enhanced with 5% of gypsum. Figure 5-3 shows the increase in heat released compared to the reference alite. In addition, the induction period is slightly increased, as seen previously for pure C_3S [6][7][9]. An enhancement is also seen in the alite doped with 3% ZnO, even higher heat released is obtained with Zn doping compared to the gypsum addition. Moreover, the alite doped with 3% ZnO with 5% gypsum shows the most increased heat released peak. This effect of the Zn-doped samples on the height of the peak is associated with the incorporation of Zn in the C-S-H structure [12][13]. A considerably extended induction period is observed in the Zn-doped alite with gypsum, where the acceleration period starts at around 37 hours. Besides, the reaction seems to be depleted as the heat released goes to zero for the entire duration of the induction period. This effect is not seen in the other samples, thus, an interaction between sulfates and zinc in solution must be considered.

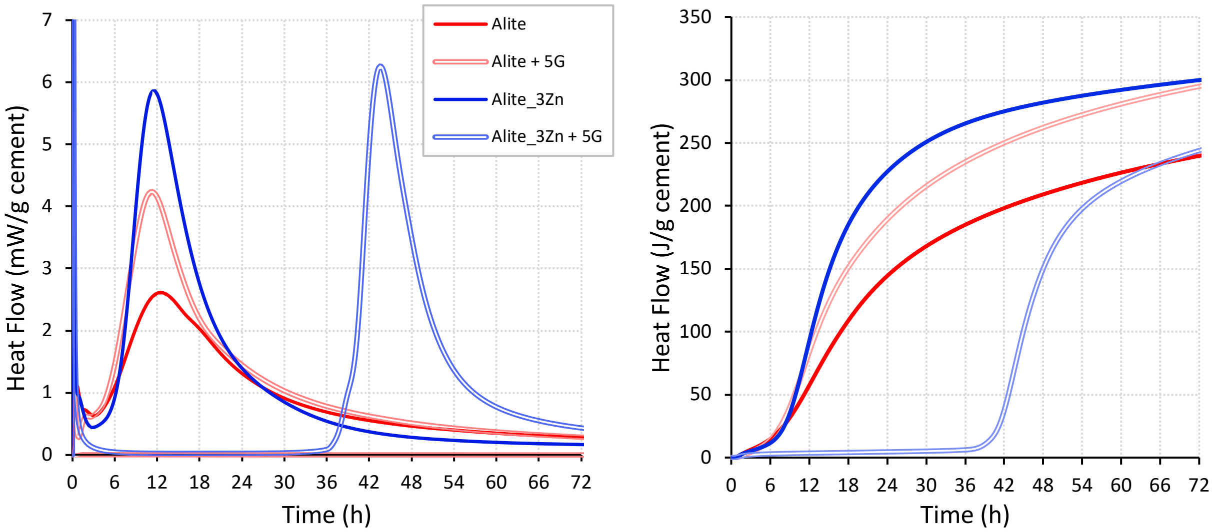

Figure 5-3: The calorimetric curve of alite system and the effect of gypsum addition.

To better understand the hydration behavior of the Zn-doped alite with gypsum addition, pore solution analysis was done at different times of the induction period. Figure 5-4 shows the concentrations of the main ions in the solution for Zn-alite with and without gypsum. The reference sample showed a decrease in Zn concentration throughout the induction period. This could explain the small extension of the dormant period compared to the alite without doping. The zinc in solution forms zinc hydroxide that later converts into calcium zincate hydrate as proposed by other researchers [2][4][14]. The presence of sulfates causes an important increase in the Zn concentration compared to the reference. This concentration decreases dramatically during the induction period. Moreover, the concentration of Al^{3+} is lower compared to the sample without gypsum and there is a slight increase at the middle point and then decreases similarly to sulfates and calcium ions.

Consequently, it seems that a certain concentration of Zn in the solution is necessary for aluminum, calcium, and sulfate to decrease. Furthermore, the pH at the start of the induction period increases for the sample with gypsum reaching similar values to the reference after the middle point (table 5-4). With these values of pH, the predominant Zn specie is $Zn(OH)_4^{2-}$ that can later convert into calcium zincate as mentioned before [15].

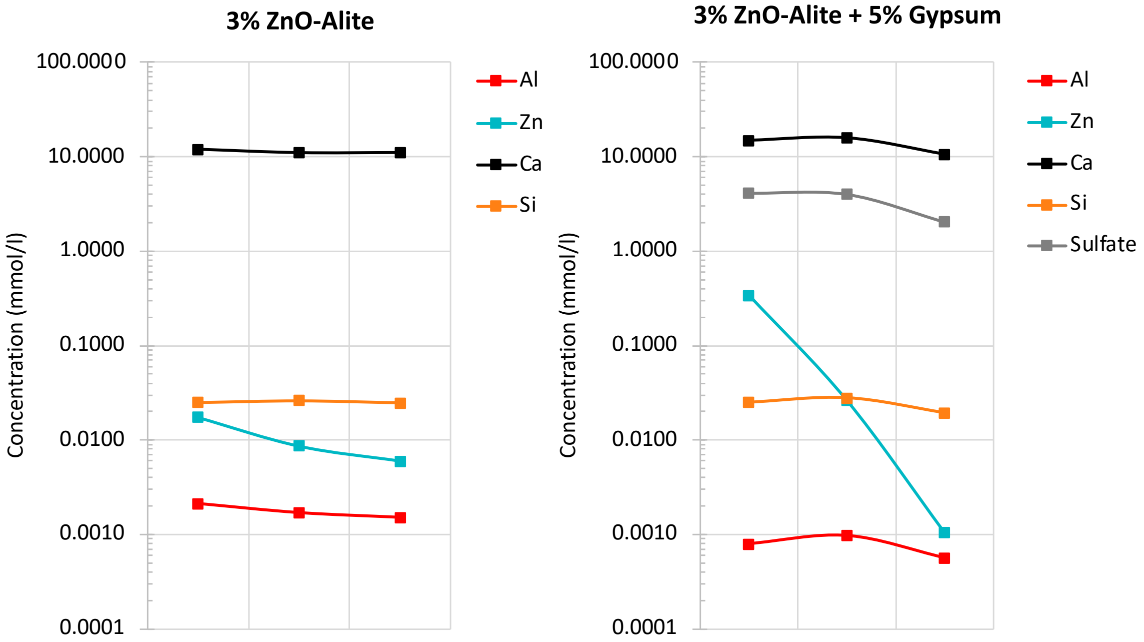

Figure 5-4: Ionic concentration in the pore solution measured at different stages of the induction period. For Zn-alite without gypsum: start = 1h, middle = 3h, and end = 6h. For Zn-alite with 5% gypsum: initial = 1h, middle = 16h, and end = 37h.

Table 5-4: The pH of the Zn-dope alite system with and without gypsum at different ages of the induction period.

		pH during induction period		
	% Gypsum	**Start**	**Middle**	**End**
Alite 3% ZnO	0	12.1450	12.2400	12.2600
	5	12.8440	12.2920	12.2920

GEMS was used to get the saturation indeces of C-S-H, ettringite, portlandite, and zincite (figure 5-5). It is worth mentioning that GEMS does not take into account the Zn that is being incorporated in the C-S-H structure. However, it gives an idea of the saturation indexes for the induction period. For the reference alite, the saturation indexes were negative for all the phases, at the beginning, middle, and at end of the induction period. In contrast, the sample with 5% gypsum showed a positive saturation index (around cero, times ten to the power of e-09) for ettringite and zincite (ZnO). Hence, the formation of ettringite is predicted to take place since the start of the induction period. With respect to Zn phases, it is difficult to have an appropriate prediction as the database does not consider all the different Zn species and phases. However, the concentration is high enough to predict zincite precipitation.

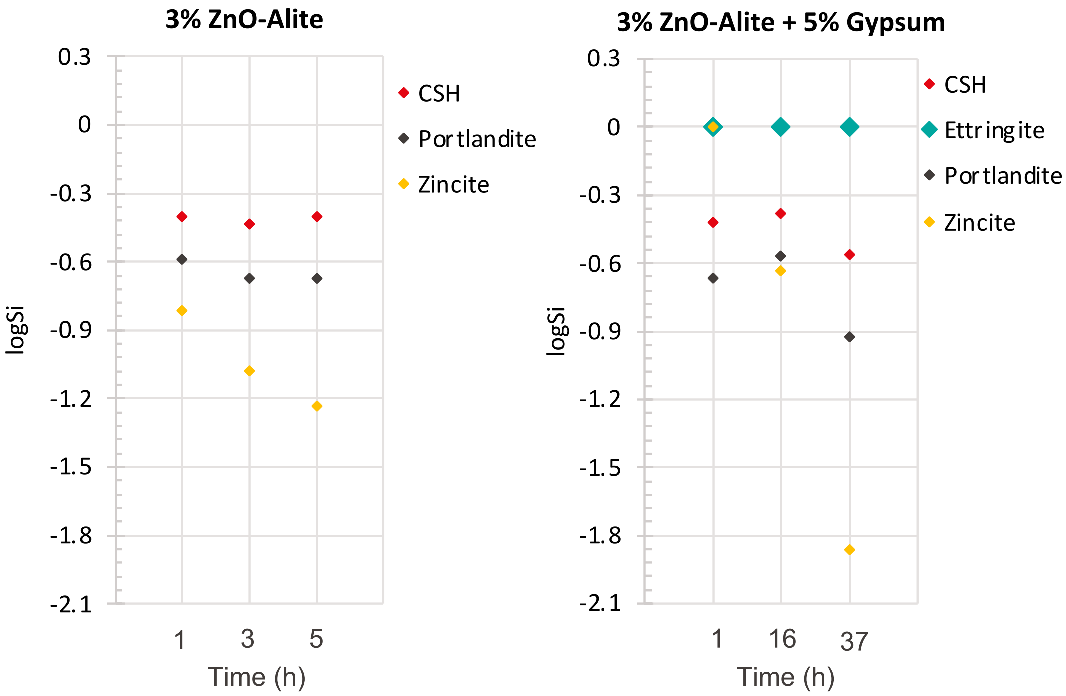

Figure 5-5: Saturation indeces of the different hydrates calculated by GEMS. With 5% of gypsum ettringite is the only phase predicted in the system.

The high concentration of Zn ions detected in the pore solution of the Zn-alite with gypsum addition may come from an additional phase formed during sintering, where the Zn is mainly concentrated. When gypsum is added, this phase dissolves first releasing Zn ions into the solution. The bright areas in SEM images in Figure 5-6 indicate the existence of such an addition phase in the alite doped with ZnO.

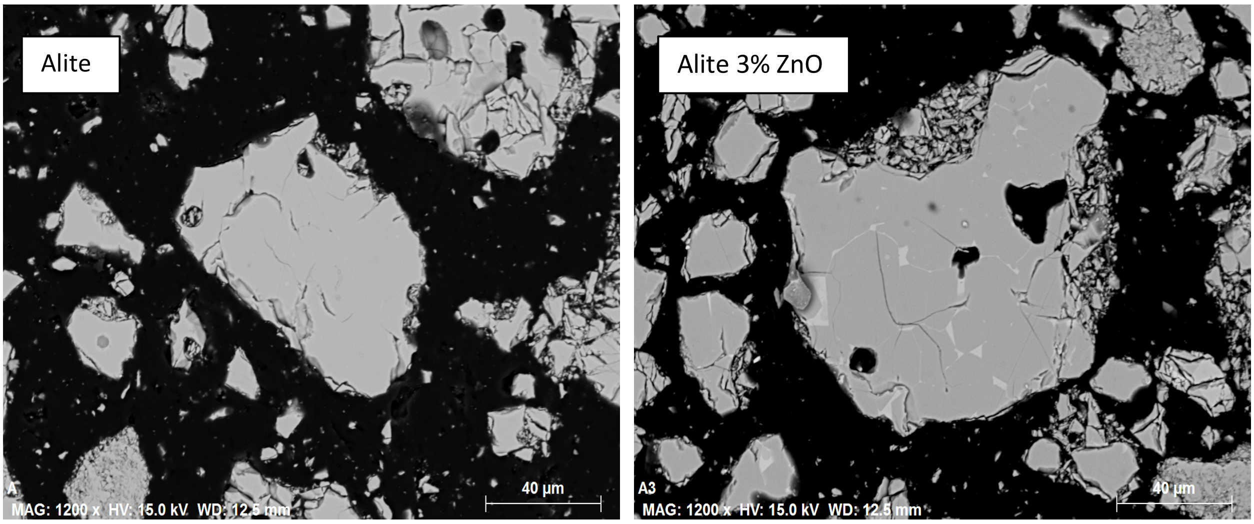

Figure 5-6: Microstructure of alite and alite doped with 3% ZnO grains.

The composition of the Zn-doped alite grains was obtained by SEM coupled with EDX. The Zn was found to be mainly concentrated in the additional phase (figure 5-7). Hence, it is possible that gypsum addition promotes the dissolution of this phase releasing Zn ions to the solution.

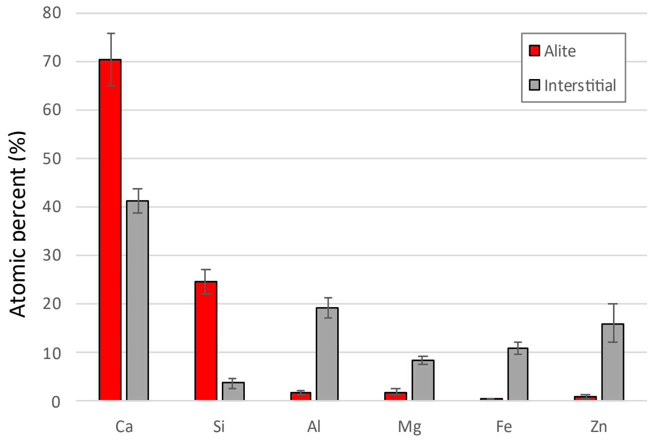

Figure 5-7: The composition of Zn-doped alite obtained by SEM-EDX. The red bars correspond to alite grains and the grey ones to the interstitial observed in figure 5.8.

Furthermore, the concentration of calcium ions in the solution of alite, alite 3% ZnO and alite 3% ZnO with gypsum addition is compared in figure 5-8, at different ages of the induction period. Higher concentration of calcium was found for the doped sample and even higher with the presence of sulfates at the start of this period, coming from the addition of calcium sulfate.

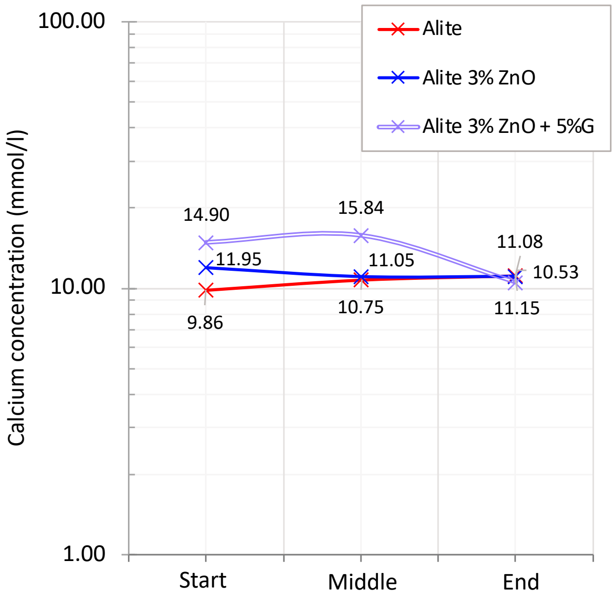

Figure 5-8: Calcium concentration in the solution of alite and alite doped with 3% ZnO thourghout the induction period. For alite: start = 1 h, middle = 2.5 h, end = 4 h. For alite 3% ZnO: start = 1, middle = 3 h, end = 6 h.

The precipitation of a Zn compound can be the cause of the retardation seen in figure 5-3. As suggested by Lieber [2], the concentration of OH$^-$ and Ca^{2+} is low and the supersaturation with respect to the C-S-H it is not reached until the conversion to calcium zincate is finish. This hypothesis has been supported by many researchers through time [3][4][14][16]. However, the pore solution results in figure 5-8 are not in agreement with the previous hypothesis. The alite without doping shows similar amounts for calcium concentration with respect to the alite doped with 3% ZnO. Therefore, together with the pH evolution in table 5-4, it seems that there is a preference of OH- for zinc ions over calcium, that might be forming

$Zn(OH)_2$, and the result is an extended induction period until the concentration of zinc in the solution is low enough for C-S-H and portlandite precipitation.

To investigate any formation of phases other than ettringite, high-resolution images were taken at the initial, middle, and end points of the induction period of the Zn-doped alite system with and without gypsum (figure 5-9).

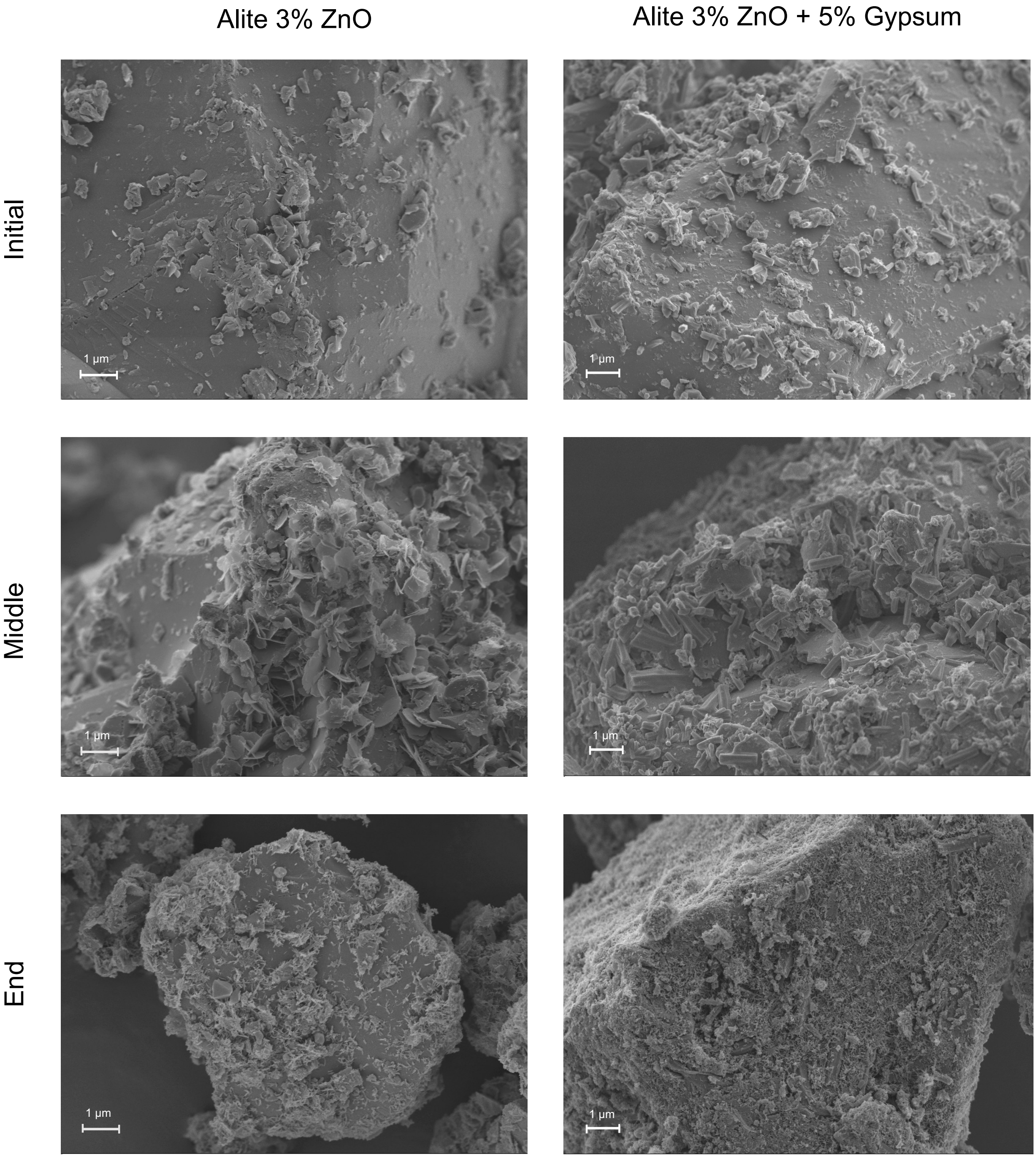

Figure 5-9: Morphology of the hydrates in Zn-doped alite, with and without gypsum at initial, middle, and end point of the induction period. For Zn-alite without gypsum: initial = 1h, middle = 3h, and end = 6h. For Zn-alite with 5% gypsum: initial = 1h, middle = 16h, and end = 37h.

The sample without gypsum showed platelets of calcium aluminate hydrates in the middle of the IP. In the absence of gypsum, these aluminate hydrates are formed and are metastable with repsect to cubic hydrogarnet (C_3AH_6) [17]. At the end of the induction period, the hydrogarnet is seen together with C-S-H that starts to nucleate and grow on the surface of the grains.

In the Zn-doped alite with 5% gypsum, ettringite is seen at the beginning of the induction period. At this point, another phase seems to be on the grain surface. After 16 hours, in the middle of the induction period, larger ettringite is seen and a higher amount of this second phase. Finally, in the end, the grains look more covered, and C-S-H is seen.

A closer look to the hydrates formed in the sample with gypsum is shown in figure 5-10. A phase is forming in the sample with gypsum, most likely to contain Zn considering the pore solution results.

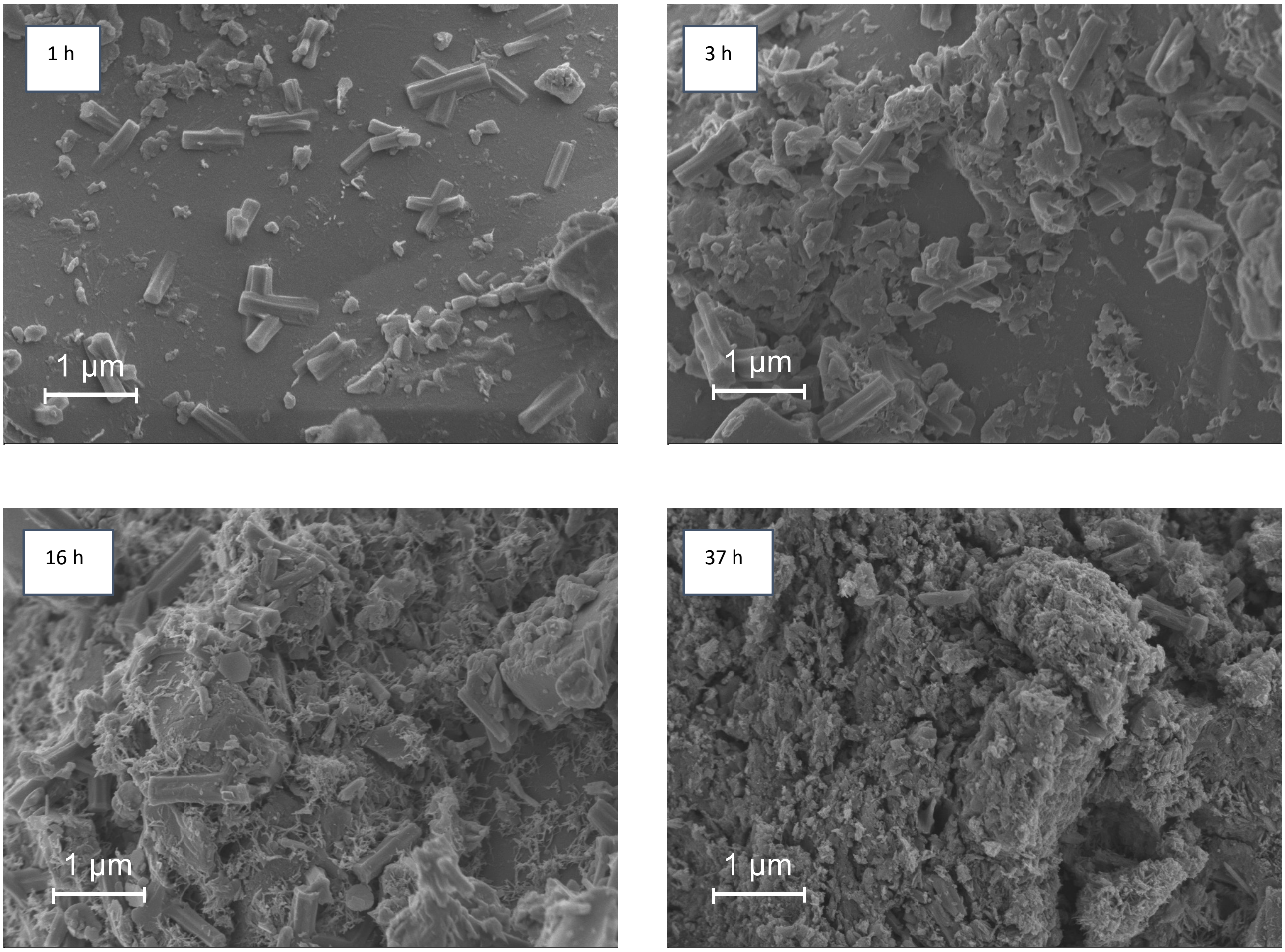

Figure 5-10: Evolution of the hydrates formed in the Zn-doped alite with gypsum addition during the induction period.

The XRD diffractograms from an in-situ experiment of the Zn-alite with 5% gypsum were qualitative compared at different ages of the induction period, 15 min, 2, 4, 8 and 18 hours (figure 5-11). The similarity of the diffractograms is evident. The ettringite peak sligthly increases and the gypsum one does not seem to change. Moreover, no calcium zincate was found nor a zinc containing phase. Hence, it is highly propable that the phase forming in the induction period corresponds to amorphous zinc compound.

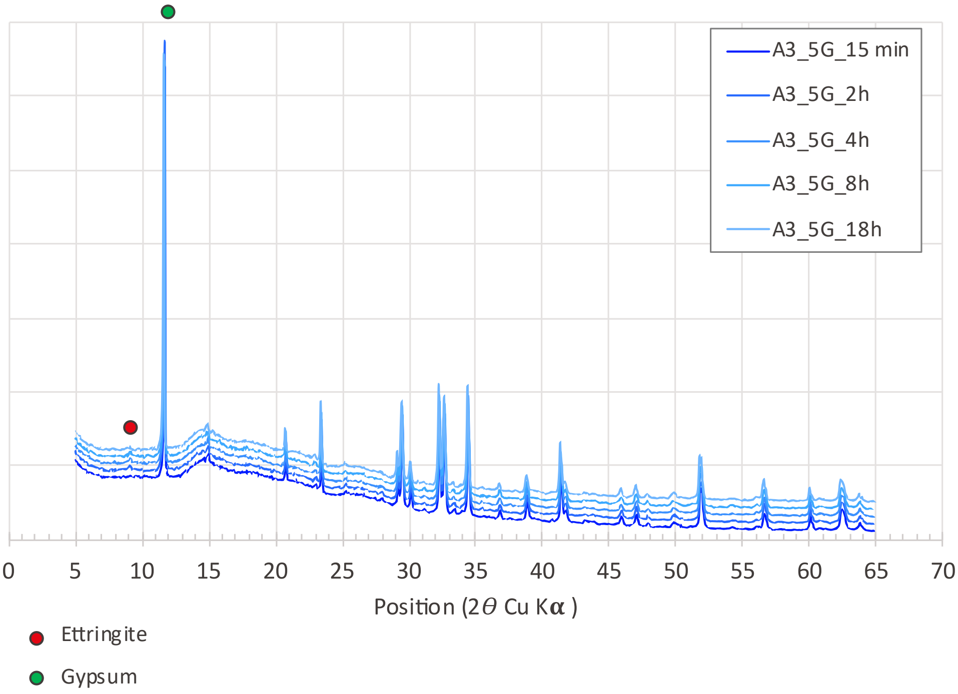

Figure 5-11: Comparison between the diffractograms at different ages of alite 3% ZnO when gypsum is added.

In line with the previous discussion, pure tricalcium silicate, undoped and doped with 3% ZnO was also studied. Figure 5-12 shows similar retardation in the sample doped with 3% ZnO and 5% of gypsum addition. This suggests that the retardation observed in the alite system is not related to aluminum and/or ettringite formation but rather to an interaction between sulfates and zinc in the solution. Moreover, it shows that the enhancement in heat released by gypsum (in the non-doped samples) can not be attributed to the formation of ettringite as stated by other researchers [7][11].

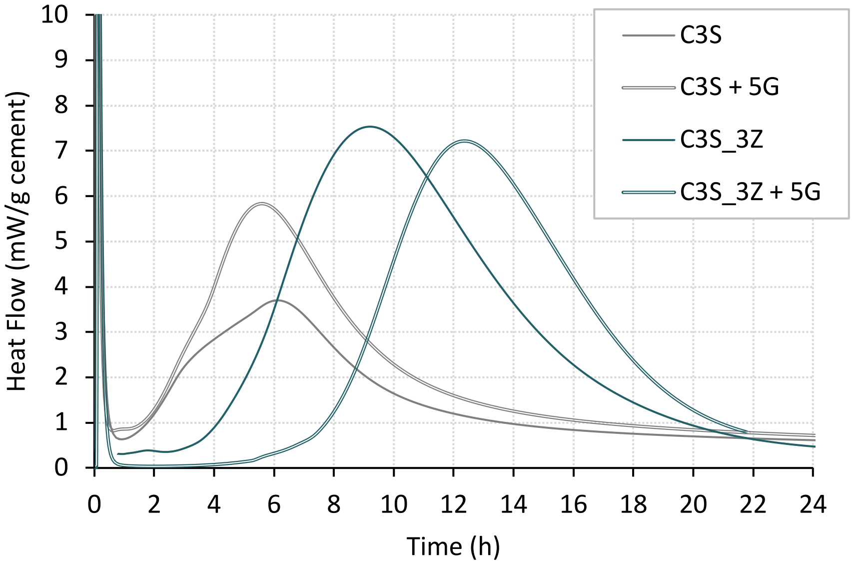

Figure 5-12: The effect of gypsum addition in the pure C_3S, reference and doped with 3% ZnO, calorimetric curves.

High-resolution SEM images were also taken for this system as shown in figure 5-13. As expected, no ettringite was found as the samples do not contain aluminum. C-S-H is seen in the sample without Zn while it is not that abundant in the doped sample.

These observations contradict the hypothesis by Arliguie et al. where they stated that when more than 2.5% of SO_3 is in the system together with C_3A, fine ettringite is formed covering the grains with an amorphous $Zn(OH)_2$ layer retarding the hydration. Even though their work is based on real cement, the alite produced for this research has aluminum that forms ettringite. No layer is found in the Zn-doped samples neither by $Zn(OH)_2$ nor ettringite. Moreover, the retardation is also observed in pure C_3S without aluminum and hence nor ettringite formation nor layer is the cause of the extension of the induction period.

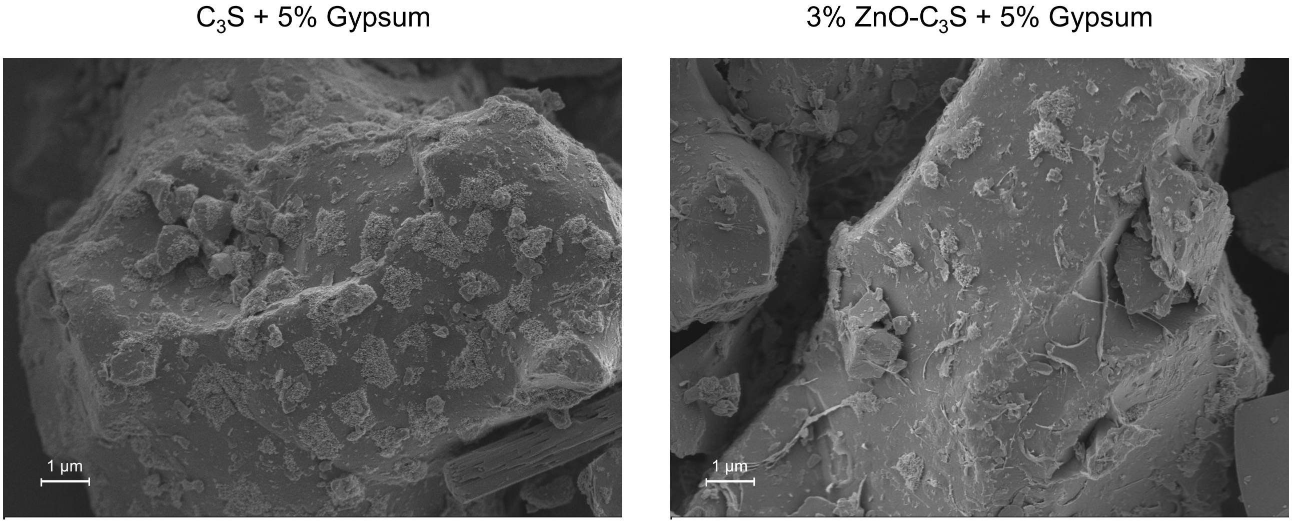

Figure 5-13: Hydrated C_3S, undoped and doped with 3% ZnO, with 5% gypsum after three hours of hydration.

5.4 Conclusions

The induction period of alite doped with 3% ZnO is dramatically extended when 5% of gypsum is added. High concentraction of Zn was found at the start of the induction period potencially coming from an interstitial material formed during the synthesis of doped alite. This phase dissolves fast in presence of sulfates and Zn ions are released to the solution.

The calcium concentration increased through the induction period until the middle point when drops. This increase contradicts the hypothesis of a calcium zincate formation as the cause of the retardation seen in Zn-doped cementitious systems.

It is proposed, based on the XRD, pore solution analysis and morphological study that the precipitation of an amorphous Zn compound$_2$ is the cause of the extended induction period observed in presence of gypsum until the concentration of zinc in the solution is low enough for C-S-H and portlandite precipitation.

Moreover, the presence of aluminum, formation of ettringite or presence of an amorphous layer is not the reason of retardation.

5.5 References

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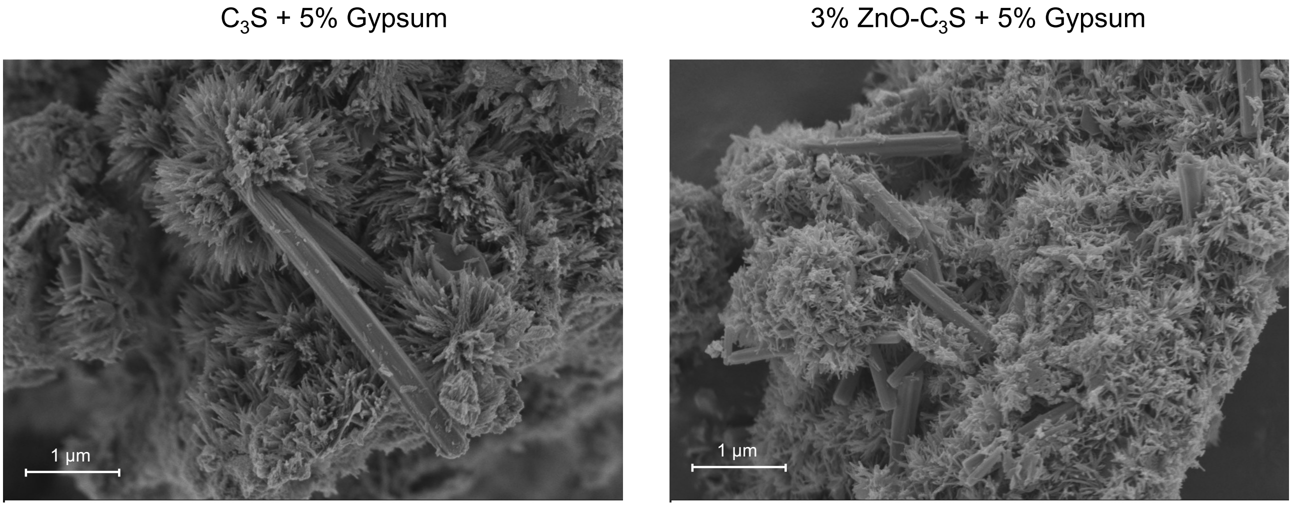
Complementary information

High-resolution SEM images were taken to the reference alite and doped with 3% ZnO, both with 5% gypsum addition after 1 day of hydration (figure 5-14). In the sample with Zn, shorter ettringite rods are seen and they seem to have the same thickness or even ticker than the alite without Zn. This evidence does not agree with Arliguie et al. [1] hypothesis. And, moreover, shows that ettringite is not responsible for the retardation in the Zn-doped sample with gypsum addition.


C_3S + 5% Gypsum

3% ZnO-C_3S + 5% Gypsum

Figure 5-14: Shorter length of ettringite rods in the Zn-doped alite eiwht gypum at one day of hydration.

However, it was intended to obtain the chemical composition of the ettringite, and the second phase formed in the alite doped with Zn in presence of gypsum. With figure 5.15 iis not possible to conclude that Zn gets incorporated in the ettringite structure or in the second phase. This type of measurement is complicated as the size of the ettringite rods is 1-1.5 μm and the interaction volume affect the characterization. Yet, if Zn is indeed in the ettringite or other phase, an accumulation of points is expected to be seen in the areas where the rods are, and this is not the case.

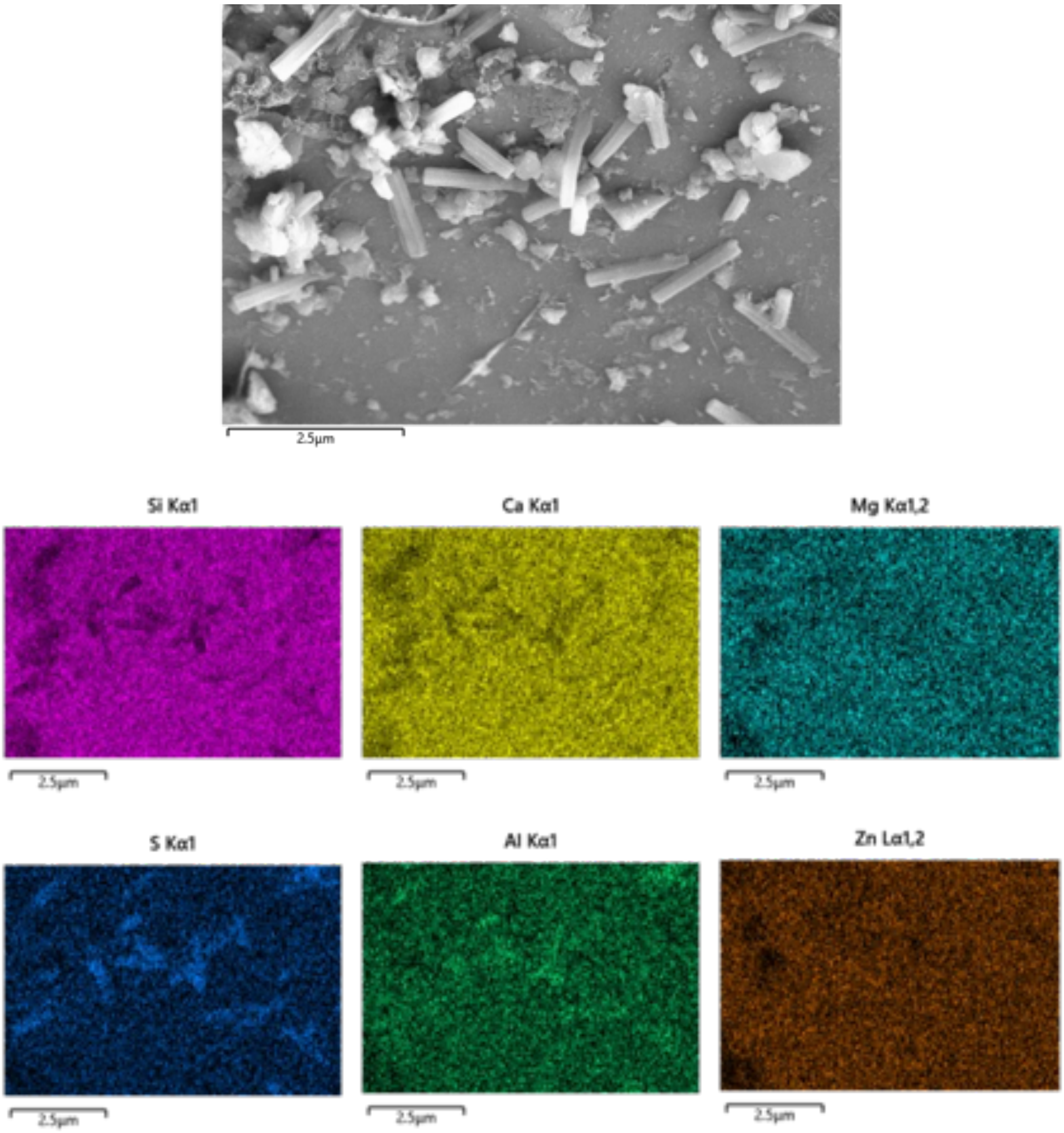


Figure 5-15: SEM-EDX mapping on the alite 3% ZnO with 5% of gypsum addition. No clear difference is found in composition a cause of the interaction volume.

References

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Chapter 6 Conclusions and perspectives

Contents

This research studied the possibilities to enhance the reactivity of cementitious systems with ZnO doping. Three systems were synthesized with minor amount of ZnO: alite, C_3A-polyclinker, and C_4AF-polyclinker. Moreover, different approaches were investigated to retain Zn in the alite phase, as this was found to be the reason for C_3S reactivity enhancement by ZnO. The dissolution of alite releases Zn ions in the solution that are incorporated into the C-S-H structure, which causes its rapid growth, as seen by Bazzoni et al. and Li et al. [1][2].

6.1 Effect of ZnO in more realistic systems

The results of this work showed that when Zn is retained in the alite phase, the hydration is enhanced. Even though the heat released may be retarded in more realistic systems, the height of the alite peak is higher in comparison to the reference. This was presumed to be caused by the Zn uptake in the C-S-H similarly to C_3S.

The Zn repartition in polyclinker is the main difference compared to alite and C_3S. Zn is mainly found in the interstitial material or as free ZnO when the dosage exceeds 3%. This preference causes massive retardation of hydration.

An amorphous phase is promoted by Zn in the C_3A-polyclinker resulting from the synthesis process. This amorphous material is based on the C_3A phase since more of this aluminate was obtained after thermal treatment at the crystallization temperature of the amorphous phase. An extra amount of gypsum was found to control its reaction and hence shorten the induction period.

However, if there is no interstitial material in the system, gypsum can also lead to severe retardation. Pore solution analysis revealed a high concentration of Zn in the solution with a higher pH in the hydration of Zn-doped alite with gypsum addition. It was proposed that the precipitation of an amorphous $Zn(OH)_2$ is the cause of the extended induction period observed in the presence of gypsum until the concentration of zinc in the solution is low enough for C-S-H and portlandite precipitation. The high concentration of Zn is believed to come from a second phase composed of Zn that dissolves faster in presence of sulfates.

The cooling rate was found to be a critical variable in the synthesis of the C_3A-polyclinker system doped with ZnO. The results from chapter 3 showed that a slow cooling rate promotes more alite and less amorphous content. Moreover, it allows a better distribution of ions, as more Zn was found in the alite phase. The hydration behavior was enhanced compared to the fast-cooling samples, supporting the hypothesis that Zn in the alite phase is beneficial for the reactivity of cementitious systems and the importance of the cooling rate in doped clinkers.

A change in the interstitial material composition to C_4AF does not avoid the retardation, but more Zn was retained in the alite phase. The free ZnO, observed in the microstructure as “white spots”, and the amorphous content seem to be more dominant in terms of hydration behavior which presence leads to more extended induction periods.

6.2 Open questions, perspectives, and applicability

Several open questions that could be further investigated are raised after the conclusion of this research.

- Why does Zn promote the formation of an amorphous phase in the C_3A-polyclinker? What is the composition and structure difference of the amorphous phase between the fast and slow-cooled samples? The interstitial material of the Zn-doped C_3A-polyclinker can be synthesized following the method used in this study and characterized by Raman spectroscopy.

- Why is gypsum causing the fast release of Zn ions into the solution? Is the addition of more or less gypsum affecting the hydration of these systems?

- Studies showed that gypsum also gets incorporated into the C-S-H structure, increasing its needle length similarly as Zn [3]. Then, what is the effect of sulfates and Zn in the C-S-H needle length? Do the C-S-H have a maximum size from which they cannot grow more? Does C-S-H have a preferred ion uptake? And how will this affect its morphology and hydration kinetics?

- How much of Zn can be incorporated in the C-S-H structure? this would help to better understand the hydration kinetics. Moreover, it is necessary to work on thermodynamic modeling to predict the behavior of the Zn doped systems. Currently, a Zn database is available in OLI and GEMS software, but some Zn salts and species are missing. The addition of thermodynamic data of the missing species is needed to have a complete database. The complexity of this study relies on the determination of the partition coefficient of Zn in the solution: how much of Zn is being retained by the C-S-H over time? How is this Zn partition changed in the presence of other ions as aluminum as sulfates? A previous work by Ziegler et al. showed that this coefficient could be estimated as a diffusion coefficient [4]. Hence, new techniques such as STEM can be used to quantify the Zn retained by C-S-H over time and estimate this coefficient.

General:

- Why ZnO? Zn was chosen because of its potential to increase cement reactivity, the quantities needed can be found in wastes, and it has low toxicity. However, the study of other elements such as nickel and copper could be explored and study the effect of the cooling rate on these systems to better understand the effect of Zn. Nickel and copper can also be found in waste and have a similar atomic radius compared to Zn.

- The alite doped with Zn showed an enhancement in hydration. Nevertheless, it is important to study hydration at later ages, and the mechanical and durability properties to have a better characterization of these Zn doped systems.

Some aspects are presented here that could be investigated and optimized if ZnO is meant to be implemented in real systems.

- The quantitative limit of Zn in cementitious systems is key to better enhance the reactivity of cementitious systems. This investigation represents a high challenge as it varies depending on the composition of the clinker. As seen, 3% ZnO enhances alite hydration, but its repartition differs depending on the composition of the interstitial material and synthesis process in a more realistic system. This quantitative limit is related to the free ZnO that remains uncombined. Thus, the synthesis of real cementitious systems with minor amount of ZnO (up to 3%) and their characterization by XRD, SEM, and isothermal calorimetry could give light to this question. Other techniques, such as pore solution analysis, can be included to investigate the hydration behavior.

- The mineralizing effect of ZnO has been reported previously [5]. Hence, lower temperatures can be used in the synthesis of these doped systems. Even though high temperature favors the ionic exchange in the melt, it is possible to obtain a similar activity at lower temperatures in the presence of Zn as high alite content was found at 1250 °C for the C_4AF polyclinker (see appendix A1). Thermodynamic modeling can be used to estimate the temperature of liquid formation depending on the raw meal composition. This also depends on the type of cementitious system.

- Furthermore, the sample size is an important factor to consider in terms of heating and cooling rate. Thus, it is crucial to investigate the points above with a synthesis closest to real clinker production.

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Appendix 1 - Influence of the synthesis temperature in C_4AF-polyclinkers doped with ZnO

High temperatures promote the diffusion of ions in the melt. Besides, it was previously shown that Zn lowers the clinkerization temperature and promotes the reaction between CaO and C_2S to form alite, thus acting as a mineralizer [1] [2]. Therefore, a synthesis temperature of 1450 °C may be higher than required in Zn-doped systems. A study by Xu Guangliang et al. showed that the activation energy for clinker formation in systems doped with ZnO could be reduced by more than 100% compared to the reference. Moreover, they obtained more Zn in the alite when the ZnO dosage was increased, but more Zn was also found in the interstitial material [3]. A polyclinker containing 90% alite and 10% C_4AF was synthesized without and with 1 and 3% ZnO at 1350 °C and 1250 °C to investigate the effect of synthesis temperature on the phase composition, the Zn repartition, microstructure, and hydration behavior of these polyclinker systems. The results are compared with the synthesis at 1450 °C presented in chapter 4.

Raw materials, synthesis, and experimental methods

The polyclinkers were synthesized by the method developed by Li et al. [4]. The raw materials used were calcium carbonate from VWR, the SiO_2 silica fumed from Sigma-Aldrich with a particle size Dv_{50} of 0.007 µm, aluminum, magnesium, and zinc oxide from MERK, and iron oxide (99.999%) from Acros Organics. They were mixed with water (double the solid mass) in a zirconia milling jar for one day and cast into carton cylinder molds. The mix was dried before calcination at 60 °C and 110 °C for one day at each temperature. Afterward, the samples were demolded and split into small pieces to avoid any damage to the furnace from a possible liquid phase and placed into platinum crucibles. The calcination was done in an 1800 °C Borel Swiss furnace operating at two different temperatures, 1250 °C and 1350 °C, at a rate of 7 °C/min, retained for three hours, and then fast cooled by air with a fan.

After calcination, the samples were ground in a stainless-steel mortar and later with a McCrone micronizing mill. 5 g of sample was mixed with 10 g of isopropanol, ground for 5 minutes, and filtered. Then, the samples were kept in a desiccator for at least two days before characterization.

The phase composition was obtained by X-Ray diffraction (XRD) with a X'Pert MPD PRO diffractometer with CuKa radiation at 45 kV and 40 mA. The analysis of the data was done with HighScore software with Rietveld refinement.

Table A1-1: Mix design for C_4AF polyclinker systems (FP = Reference, FP_1 and FP_3 polyclinkers doped with 1 and 3% ZnO, respectively).

System/ Raw materials (%)	CaO	SiO_2	Al_2O_3	MgO	Fe_2O_3	ZnO
FP	66.50	23.83	3.11	1.72	4.85	0.00
FP_1ZnO	65.84	23.59	3.08	1.70	4.80	1.00
FP_3ZnO	64.51	23.12	3.02	1.67	4.70	3.00

Laser diffraction was used to measure the particle size distribution (PSD) with a Malvern MasterSizer S with the SHE_3 optical model (n=1.7, k=0.1, n=1.39). The specific surface area was determined by nitrogen adsorption-desorption obtained with a Tristar II plus from Micromeritics following the Brunauer–Emmett–Teller 5 points method (SSA-BET).

The hydration curves were studied by isothermal calorimetry at 20 °C. An IKA Eurostar 40 mixer was used to mix the samples with a w/c = 0.5 speed of 1600 rpm for 2 min. No gypsum was added considering the low percentage of C_3A and the retarding effect seen in Zn-doped alite and C_4AF-Polyclinkers.

The amount of Zn in alite was acquired by scanning electron microscopy (SEM) coupled with energy dispersive X-rays (EDX). The powder samples were mixed with resin, polished, and carbon-coated. A microscope FEI Quanta 200 with a back-scattered electrons (BSE) mode was used operating at 15 kV.

Results and discussion

As a general overview, the phase quantification in table A1-2 shows that more C_3S is obtained with an increase in synthesis temperature. This effect can be associated with an increase in the liquid phase promoted at higher temperatures along with a decrease in its viscosity, facilitating ion transport. [5] Furthermore, less amorphous tends to form compared to the lowest temperature. This amorphous content decreases with Zn doping, except for the FP_3 synthesized at 1250 °C, and it is not seen in the samples synthesized at 1450 °C (see chapter 4, table 4-4). Moreover, the highest percentage of belite was detected in the samples at 1250 °C. This temperature is where the transition between C_2S and C_3S occurs; hence, below it, C_3S decomposes in free CaO and C_2S. The doped samples showed less belite than the reference, while the amount of free lime was kept low. This indicates that ZnO acts as a mineralizer since a higher amount of C_3S was obtained. This effect is not seen in the sample fired at 1350 °C, as the C_3S decreases with Zn doping. However, this decrease is more pronounced in samples fired at 1450 °C.

Table A1-2: Phase quantification of C_4AF-Polyclinker synthesized at 1250 °C and 1350 °C.

	1250 °C			**1350 °C**		
	FP	**FP_1**	**FP_3**	**FP**	**FP_1**	**FP_3**
C_3S	70.30	74.60	71.90	78.00	78.30	77.10
C_2S	7.00	3.90	3.50	-	-	1.00
C_3A	0.70	0.20	-	-	0.90	-
C_3A - O	-	-	1.60	-	-	1.40
C_4AF	10.50	11.50	9.50	11.80	12.20	12.30
Free lime	0.40	0.40	0.80	0.64	-	0.01
ZnO	-	-	0.60	-	0.05	0.67
Amorphous	11.10	9.30	12.20	9.50	8.50	7.40

A trend is not seen in either the average particle size (Dv_{50}) or in the specific surface area. However, the finer particles were obtained for the samples synthesized at 1250 °C.

Table A1-3: The average particle size (Dv_{50}) and specific surface area (SSA),

		Dv50 (µm)	**BET SSA (m^2/g)**
1250 °C	FP	17.51	1.606
	FP_1ZnO	10.79	1.2406
	FP_3ZnO	17.51	0.8537
1350 °C	FP	12.92	0.904
	FP_1ZnO	12.69	1.4759
	FP_3ZnO	15.54	0.8404

The microstructure of the samples is compared in Figure A1-1. The reference system without doping looks very similar in both temperatures. When Zn is added, white spots are observed in the samples calcined at 1350 °C, corresponding to free ZnO and, as seen previously in [5] and [6]. These spots are more visible with a 3% ZnO dosage. The white spots are not seen for the sample synthesized at 1250 °C, but free lime areas are observed. The interstitial material looks different as well. The samples calcined at higher temperatures exhibit more interstitial and, more important, this interstitial is more complex as Zn is added. Different phases constitute this interstitial in the sample with 3% ZnO fired at 1350 °C. These phases correspond to C_4AF, C_3A, and free ZnO.

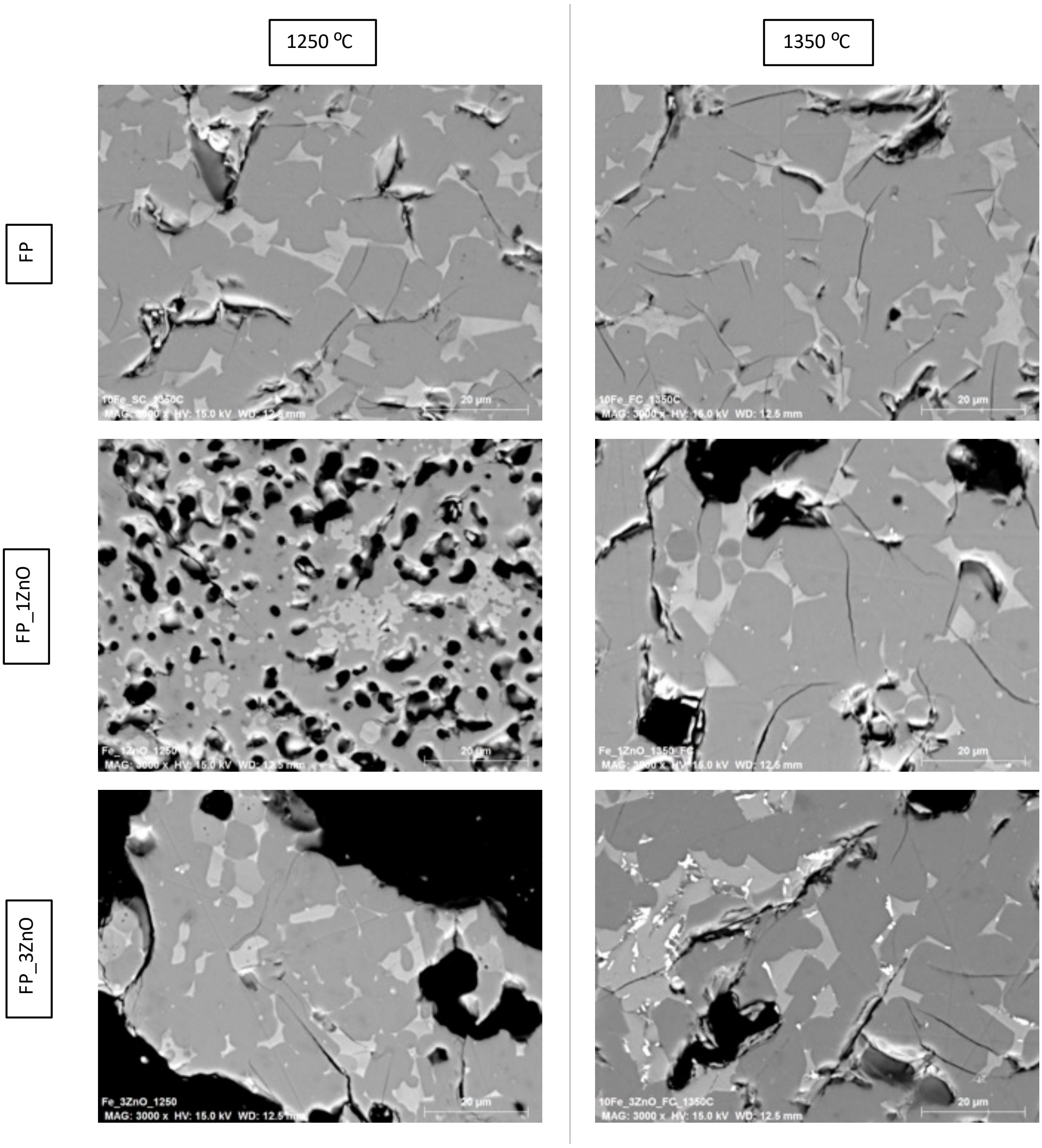

Figure A1-1:Microstructure comparison of the FP system synthesized at two different temperatures, left = 1250 °C and right = 1350 °C.

The amount of Zn in the alite was measured by SEM-EDX point analysis. The results show a tendency of more Zn in alite as more ZnO was used as raw material, as seen in previous chapters. More Zn was found in alite in the case of 1250 °C, which agrees with the XRD results. Zn takes calcium sites in alite and hence promotes its formation.

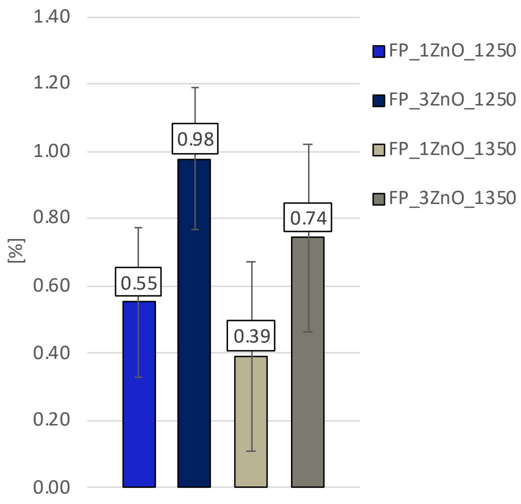

Figure A1-2:The estimated amount of Zn in alite by SEM-EDX point analysis on alite grains of the FP system synthesized at 1250 °C and 1350 °C.

The hydration behavior is shown in figures A1-3 and A1-5 for the samples calcined at 1250 °C and 1350 °C, respectively. In general, the system at lower temperatures seems to behave better in terms of alite peak positioning. Extended induction periods are seen at higher temperatures. This indicates that even though this system has less C_3S (table A1-2), the increased amount of Zn in alite has a positive effect. However, the extension of the induction period is also related to the white dots observed in figure A1-1 for the system at 1350 °C. While the quantification of ZnO by XRD was very low, it may be enough to affect the reaction. Zn in solution may form a Zn compound retarding the supersaturation needed for C-S-H to grow; hence prolonged induction periods are observed as proposed by other researchers [7][8][9][10].

Doping with 1% ZnO does not enhance the reaction in any case. At higher temperatures, the heat released is enhanced but retarded. Moreover, the curve of the sample at 1250 °C has a second peak at around 60 hours. Further investigation is needed to better understand this, but it is probable that Zn can also enhance belite reaction, and this second peak is the result.

When doping with 3% ZnO, the peak height is increased in both cases. Nevertheless, the cumulative heat for the doped samples at 1250 °C is lower than the reference. This amount of ZnO in the raw materials seems to be higher than the quantitative limit of Zn in these systems. This limit may be somewhere between 1 and 3% ZnO and must be considered in the future.

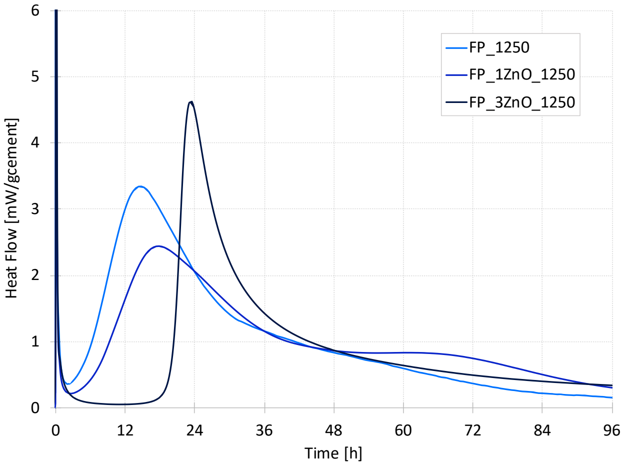

Figure A1-3: Calorimetric curves of the FP system synthesized at 1250 °C.

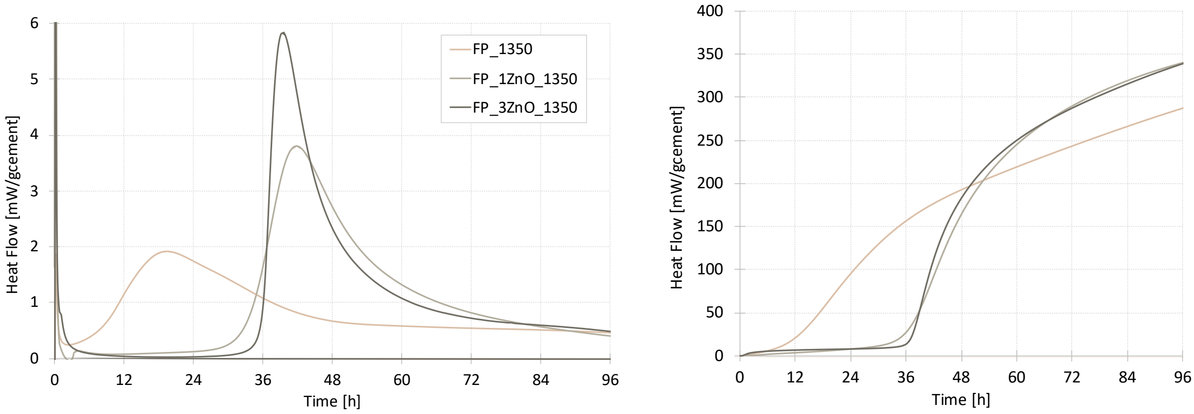

Figure A1-4: Calorimetric curves of the FP system synthesized at 1350 °C.

Conclusions

A calcination temperature of 1250 °C and 1350 °C for the synthesis of 10% C_4AF-polyclinkers doped with ZnO was studied. It affects the phase assembly, microstructure, Zn repartition, and thus hydration behavior. Zn showed a mineralizing effect in samples synthesized at 1250 °C, and more Zn was found in alite for these samples. A second peak was observed at 1% ZnO doping, which may be associated with belite, but further studies are needed to confirm this.

The samples synthesized at 1350 °C exhibited higher heat released with an extension of the induction period related to the white spots seen in their microstructure corresponding to free ZnO.

The quantitative limits of ZnO in these systems need further investigation, but they could be somewhere between 1 and 3% ZnO.

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Curriculum Vitae

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PERSONAL INFORMATION

Date of Birth	05/05/1992
Nationality	Venezuelan
Languages	Spanish (native speaker) English (advanced user) French (intermediate user, B1) Portuguese (intermediate user, B1)

EDUCATION

2018 - Present **Ph.D candidate, Laboratory of Construction Materials (LMC)**

EDMX Materials Science and Engineering
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE (EPFL), Lausanne, Switzerland
Thesis: *Effect of ZnO on Alite and Cement Hydration*

2010 - 2017 **Materials Engineer**

UNIVERSIDAD SIMON BOLIVAR (USB), Venezuela
Thesis: *Impact of Temperature on Belite Cements Additivated with Nano-silica and Nanoalumina*
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1998 - 2010 **Primary and Secondary School**

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PROFESSIONAL EXPERIENCES

2018 - Present **ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE (EPFL)**

Research assistant
Responsible for SEM and Masonry lab work
Responsible for SEM, N_2-adsorption, Furnaces
Supervision of two master project students

Mar 2017 - Jun 2017

CIPLAST S.C.A, Caracas, Venezuela

Head of Quality Control

Management, planning, coordination, daily checks of the production process: raw material, dyes, packaging material, and product in process and finished both in production lines and before dispatch. Mechanical and functional tests, following COVENIN-ISO 9001

Jul 2016 – Nov 2016

INTEVEP - PDVSA Petróleos de Venezuela S.A.

Research intern

Development of environmentally friendly cement, resistant to high temperature and pressures for oil wells

Jul 2014 – Aug 2014

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Quality Control Intern

Update the dimensions of the entire production

PUBLICATIONS

2019 **A. Teixeira**, K. Scrivener. The effect of zinc on alite and cement hydration. 39th Cement and Concrete Science Conference, 9th-10th September 2019, University of Bath, UK (Proceeding publication).

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2018 O. Corona, **A. Teixeira**, A. Balza. Belite cement: an environmental and industrial alternative. INVESTIGATIO No. 10, pp. 10-17.

SKILLS

Characterization Techniques: Isothermal calorimetry, scanning electron microscopy (SEM) in secondary electrons and backscattered electrons mode, energy dispersive analysis (EDS), Nitrogen adsorption (N_2-BET), X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), particle size distribution (PSD).

Experimental: Mechanical tests, mortar preparation, clinker synthesis (lab scale), 1800 °C furnaces, polishing, grinding.

IT: Edxia, Origin, X'Pert HighScore, ESPIRIT

Soft skills: Teamwork, Adaptability, Management, Marketing, Networking

INTERESTS & HOBBIES

Sports	Hiking, cycling, swimming, kung fu, skiing, fitness, surfskate.
Reading	Poke the box, The Monk Who Sold his Ferrari, Thinking Fast and Slow…
Social	UNIV HACK 2021 and 2022 as team leader Bike to work
Others	Dance (bachata, salsa) and piano