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**Abstract:**

Calcium sulfoaluminate (C\$A) cement is a binder of increasing interest to the cement industry and as such is undergoing rapid development. Current formulations do not contain alite; however, it can be shown that hybrid C\$A-alite cements can combine the favourable characteristics of Portland cement with those of C\$A cement while also having a lower carbon footprint than the current generation of Portland cement clinkers.

This paper presents two results on the formation of alite calcium sulfoaluminate (a-C\$A) clinkers. The first is a thermodynamic study which demonstrates that the production of a-C\$A clinker is possible without the use of mineralizers such as  $\text{CaF}_2$ , doping with foreign elements such as barium and strontium, or using multiple stages of heating to produce ye'elimite. It is established that a-C\$A clinker can be readily produced in a standard process by controlling the oxygen and sulfur dioxide fugacity in the atmosphere. This allows for the stabilization of ye'elimite to the higher temperatures required for alite stability.

The second result establishes that when using fluorine to mineralise a-C\$A clinker production at  $1250^\circ\text{C}$ , the iron content in the clinker is also an important variable. Although the exact mechanism of alite stabilisation is not known, it is shown that alite formation increases with the combination of  $\text{CaF}_2$  and  $\text{Fe}_2\text{O}_3$  in the mix.

**Keywords:** Sustainability; Materials technology; Climate change, Clinkering/clinkering reactions; Mineralisers; Phase equilibria; Special cements; Sulfate-based cements; Ferrite

**List of notation**

<b>Pp</b>	<b>Partial pressure</b>
<b>a-C\$A</b>	<b>alite calcium sulfoaluminate</b>

The cement oxide notation used in this work is as follows:

<b>C</b>	<b>CaO</b>
<b>S</b>	<b>SiO<sub>2</sub></b>
<b>A</b>	<b>Al<sub>2</sub>O<sub>3</sub></b>
<b>F</b>	<b>Fe<sub>2</sub>O<sub>3</sub></b>
<b>\$</b>	<b>SO<sub>3</sub></b>
<b>c</b>	<b>CO<sub>2</sub></b>

## 1. Introduction

Cement is the most manufactured product on earth by mass with worldwide cement production at approximately 4.2 billion metric tons in 2015 (Jewell and Kimball 2015). Portland cement (PC) has been used over the past century as the primary binder in almost all our construction infrastructure. Unfortunately, its manufacture is accompanied by the emission of carbon dioxide and scientific evidence indicates that these emissions are damaging our planet. The production of cement is responsible for 8% of global man-made CO<sub>2</sub> emissions (Olivier, Janssens-Maenhout et al. 2016). More than 60% of the CO<sub>2</sub> emissions associated with traditional cement manufacture are generated from the embodied carbon liberated upon ignition of the CaCO<sub>3</sub> sources used; while, the remainder are mainly from the combustion of fossil fuels required for the pyro-processing of the raw materials and less than 10% are from the use of electricity required mainly for grinding (Gartner 2004). Climate change mitigation is one of the major global challenges today and moving cement manufacture to a more sustainable process is an essential part of this; thus, the cement industry is looking for novel low-carbon binders. The challenge is that different cements have different properties and the future of the construction industry may have to shift towards using application-specific cements rather than looking for a universal alternative binder; thus, the development of novel binders is essential. Novel binders must have a lower carbon footprint while retaining key desirable criteria: (i) they can be produced from readily available and inexpensive raw materials, (ii) they exhibit properties such as high early strength gain equivalent to or better than PC, and (iii) their production is a one stage process using the rotary kiln and requiring minimal capital investment. A promising novel mineral formulation often suggested but not routinely achieved in practice is an alite calcium sulfoaluminate (a-C\$A<sup>1</sup>) formulation. In this system, ye'elimite supplements alite and replaces, in part, other clinker phases; thus, it can also be referred to as a modified Portland cement. Ye'elimite based cements are more environmentally friendly than PC mainly due to a lower lime content (Hanein, Galvez-Martos et al. 2018). As shown in Tab. 1, ye'elimite has the lowest CO<sub>2</sub> content in the raw-material by mass compared to the major phases in PC; thus, replacing part of PC clinker by ye'elimite will reduce the overall carbon footprint of the clinker, provided that ye'elimite can be used as a direct substitute for the other phases on a mass basis.

**Table 1: Specific raw material CO<sub>2</sub> emissions of cement clinker phases, adopted from Ref. (Hanein, Imbabi et al. 2016).**

Phase	Raw materials	g CO <sub>2</sub> / g phase
<b>C<sub>3</sub>S</b>	3Cc + S	0.578
<b>C<sub>2</sub>S</b>	2Cc + S	0.511
<b>C<sub>3</sub>A</b>	3Cc + A	0.489
<b>C<sub>4</sub>AF</b>	4Cc + A + F	0.362
<b>C<sub>4</sub>A<sub>3</sub>\$</b>	3Cc + 3A + C\$	0.216

In attempting to establish a recipe to ensure a smooth transition from the manufacture of PC to the cement of the future, a-C\$A cement is promoted due to the following arguments:

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<sup>1</sup> In this work, a-C\$A clinker refers to a clinker that contains both alite and ye'elimite as major phases. The clinker can also contain other phases such as belite and ferrite.

- It has potential to lower CO<sub>2</sub> emissions compared to PC due to the CO<sub>2</sub> reduction associated with 1) ye'elimite replacement in traditional clinker, and 2) an increased blending of clinker with calcium sulfate required for the production of ettringite from ye'elimite during hydration; thus reducing the clinker factor.
- It has a unique clinker composition with the combination of both alite (C<sub>3</sub>S) and ye'elimite (C<sub>4</sub>A<sub>3</sub>S) into one clinker. These are the phases responsible for most of the early strength development in their respective traditional cements, PC and calcium sulfoaluminate (C\$A) cement.
- It is believed that a-C\$A cement can help bridge the gap in reactivity between ye'elimite and slow-reacting belite that is responsible for mechanical shortcomings observed in belite calcium sulfoaluminate clinkers. For example, it has been shown that the strength development at 1-7 days, is enhanced in belite-alite-ye'elimite systems when compared to belite calcium sulfoaluminate systems (Londono-Zuluaga, Tobón et al. 2017).
- Alite-C\$A cement could prove to be an interesting strategy by industry to bridge the transition from PC to C\$A-based cements as it demonstrates commonality with PC which is by far the most trusted and well-understood construction material.
- The presence of ye'elimite in the clinker could improve the grinding process of the clinker as it is considered easier to grind; thus, further energy and carbon savings can be realised.
- Industrial by-products containing alumina, e.g., red mud and ladle slag can be used as raw materials for production of a-C\$A clinker.
- Cheaper sulfur-containing "sour" fuels can be used in pyro-processing as the sulfur can be incorporated in to the clinker from the gas phase to produce ye'elimite (Hanein, Galan et al. 2016).
- It can be used in specific applications demanding fast setting times such as structure repairs and/or waste stabilization and encapsulation.

One of the major hindrances in the development of a-C\$A cement is its difficult production process. The major issue is that, under conventional processing conditions, stoichiometric alite (C<sub>3</sub>SiO<sub>5</sub>) is only stable at temperatures above 1250°C and forms rapidly only at temperatures above 1400 °C. On the other hand, at high temperatures, the sulfur content of ye'elimite is increasingly volatile and ye'elimite decomposes incongruently evolving SO<sub>2</sub> and O<sub>2</sub> gas at temperatures above 1300 °C (Hanein, Elhoweris et al. 2015).

This study briefly reviews the current practice used to manufacture a-C\$A clinker and presents two novel routes to producing it. The first is a thermodynamic assessment showing that control of the process atmosphere can create an environment, readily attainable in conventional rotary kilns, in which alite and ye'elimite coexist. The second is an experimental study showing the importance of clinker iron content when producing a-C\$A cement through fluorine mineralization to enhance the stability range of alite.

## 2. Current methods for manufacture of a-C\$A clinkers

Recently, the concept of a-C\$A clinker has attracted interest and a few routes to the production of this binder have been proposed and are reviewed here.

### 2.1. Blending PC and C\$A cements

A simple way to obtain a clinker containing both alite and ye'elimite is to blend Portland cement with C\$A cement. Studies on blends of Portland and C\$A cements generally focus on blending ratios and the hydration mechanisms. Chaunsali and Mondal (Chaunsali and Mondal 2015) investigated the influence of C\$A cement content on expansion and hydration behaviour of the blends. They found that increasing the content of C\$A within the blends increased the expansion mechanism due to the crystallization stress caused by the supersaturation of ettringite and they suggested a replacement of less than 30% C\$A in PC as they predict tensile failure in blends with 30% C\$A replacement. Trauchessec et al. (Trauchessec, Mechling et al. 2015) presented PC and C\$A cement blends as binders which can be customised for specific applications by varying the proportions of each.

### 2.2. Introducing foreign elements

#### 2.2.1. Calcium fluoride and sulfate

PC is made by firing a calcium carbonate source such as limestone with siliceous clays and/or shales containing oxides of aluminium and iron at temperatures of  $\approx 1450^\circ\text{C}$ ; the high temperature is required to produce alite (Taylor 1997). Several studies (Moir and Glasser 1992, Qing, Jianmin et al. 1992, Masood, Mehrotra et al. 1993, Odler and Zhang 1996, Zhang and Odler 1996, Raina and Janakiraman 1998, Engelsen 2007) have demonstrated that the burnability of PC clinker can be improved by combining both calcium fluoride and sulfate. In particular, it was found that the combination of calcium fluoride ( $\text{CaF}_2$ ) and calcium sulfate ( $\text{CaSO}_4$ ) was the most effective mineralizer for lowering the clinkering temperature of PC and accelerating the reaction of free CaO mainly to form alite (Moir and Glasser 1992, Ali, Gopal et al. 1994, Odler and Zhang 1996, Snellings, Schepper et al. 2012). However, fluorine also reacts forming an apatite-like structure, fluorellestadite ( $\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3\text{F}_2$  or  $3\text{C}_2\text{S}.3\text{C}\$. \text{CaF}_2$  in cement notation), that decomposes above  $1250^\circ\text{C}$  into a liquid phase, belite ( $\text{C}_2\text{S}$ ) and gases ( $\text{SO}_2$  and  $\text{O}_2$ ) (Blanco-Varela, Vázquez et al. 1986, Gimenez-Molina, Blanco et al. 1992, Giménez-Molina and Blanco-Varela 1995, Blanco-Varela, Palomo et al. 1997, Blanco-Varela, Palomo et al. 2010, Pajares, De la Torre et al. 2012). Fluorellestadite is known to be an inert phase during hydration and recommendations are generally to reduce its presence in the final clinker. Shame and Glasser (Shame and Glasser 1987) showed that fluorine in conjunction with aluminium are incorporated into the alite crystal structure. The resulting solid solution stabilised alite to as low as  $\approx 1050^\circ\text{C}$  without formation of fluorellestadite. The observed maximum substitution of fluorine in alite was  $x = 0.15$  and the solid solution had the general formula  $\text{Ca}_3\text{Si}_{1-x}\text{Al}_x\text{O}_{5-x}\text{F}_x$ . In addition, Tran et al. (Tran, Herfort et al. 2009) also demonstrated that in white Portland cement, (with no calcium sulfoaluminate clinker phase), fluoride ions are incorporated in the alite phase. Initially, the single stage production of a-C\$A clinker was believed not possible due to the temperature gap in their stability. On the one hand, the limit set by the decomposition temperature of  $\text{C}_4\text{A}_3\$\ (\approx 1300$

°C) and on the other, the higher formation temperature of  $C_3S$  in conventional cement manufacturing process configurations. Londono-Zuluaga et al. (Londono-Zuluaga, Santacruz et al. 2015, Londono-Zuluaga, Tobón et al. 2017) demonstrated the production of a-C\$A clinker with around, by weight, 60%  $C_2S$ , 14%  $C_3S$ , and 10%  $C_4A_3$ \$. This was achieved by adding 0.9% of  $CaF_2$  and an excess of sulfate in the mix, sintered at 1300°C for 15 minutes.

With the aim of utilizing red mud, an industrial by-product, Duvallet et al. (Duvallet 2014, Duvallet, Zhou et al. 2015, Robl, Duvallet et al. 2015) used  $CaF_2$  to mineralise an a-C\$A clinker and reported the successful production of a high-iron containing alite-C\$A-ferrite clinker. The formulation was designed to maximise the amount of ferrite in the clinker while also developing acceptable compressive strengths. They produced clinker compositions of, by weight, 13-38%  $C_3S$ , 14-38%  $C_2S$ , 16-21%  $C_4A_3$ \$, 4-47%  $C_4AF$ , and 0-2%  $C$ \$.

### **2.2.2. Barium and strontium**

Another method for the synthesis of a-C\$A clinker involves stabilizing ye'elinite to higher temperatures by doping with divalent elements. Studies have been conducted showing partial replacement of calcium in ye'elinite by either strontium or barium, thus stabilising it to temperatures approaching traditional PC clinkering temperature (Xin, Jun et al. 2000, Lu, Li et al. 2012, Chang, Shang et al. 2015).

### **2.2.3. Titanium, copper and zinc**

Liu et al. (Liu, Li et al. 2013) studied the influence of titanium dioxide ( $TiO_2$ ), along with  $CaF_2$ , on the mineral formation of a-C\$A cements. They claimed that a small amount of  $TiO_2$  ( $\leq 1\%$ ) improves the burnability of the raw mix, by decreasing the free lime content and promoting formation of both  $C_3S$  and  $C_4A_3$ \$. However, increasing contents of  $TiO_2$  showed an opposite effect. Copper and zinc in the raw mix were also reported to increase melt formation and act as fluxes. Ma et al. (Ma, Shen et al. 2006) reported that the addition of  $CuO$  to the raw meal improved the clinker burnability and promoted a-C\$A cement manufacture; while, Zea-Garcia et al. (Zea-Garcia, De la Torre et al. 2017) used zinc sulfate and  $CaF_2$  as a mineraliser combination for the manufacture of a-C\$A cements.

## **2.3. Re-firing of PC**

Ma et al. (Ma, Snellings et al. 2013) reported a two stage route for a-C\$A clinker manufacture through a second, lower-temperature, firing of conventional PC clinker at 1250°C. However, the results only show the formation of a clinker with less than 4% by weight  $C_4A_3$ \$.

## **3. Controlling the atmosphere to stabilize ye'elinite to higher temperatures**

The available routes for a-C\$A clinker manufacture, while feasible, do not represent a desirable starting point owing to difficulties of quality control in production. The title paper describes a novel single stage alternative process for a-C\$A clinker which can achieve high ye'elinite yields.

The successful production of C\$A-based cement, using sulfur both as a fuel and as a source of clinker sulfur trioxide, has already been demonstrated (Hanein, Galan et al. 2016, Hanein, Galan et al.

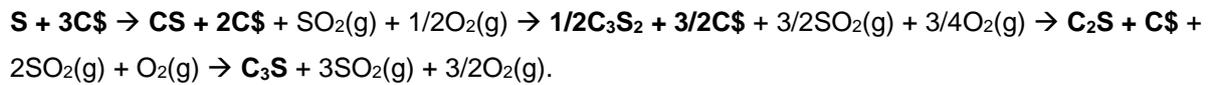
2017). These works not only prove that C\$A cement can be made at scale through solid-gas reactions but also highlight the importance of controlling the kiln atmosphere (Galan, Hanein et al. 2017). This study uses a thermodynamic assessment to show that the atmosphere can be controlled to stabilise ye'elimite to higher temperatures such that alite and ye'elimite can be produced simultaneously in a single stage without the use of dopants and/or mineralisers.

### 3.1 Thermodynamic model

The thermodynamic assessment uses a previously developed model and database (Hanein, Glasser et al. 2015) updated as discussed by (Hanein, Galan et al. 2017). Thermodynamic data for ye'elimite have also been recently updated (Hanein, Sant et al. 2018). The calculations and phase diagrams are constructed from free energy minimisation under the constraint of an elemental balance and all gases are assumed ideal; thus, fugacity can be equated with partial pressure. Previous works (Hanein, Galan et al. 2016, Galan, Elhoweris et al. 2017, Hanein, Galan et al. 2017) identified three important variables for the manufacture of C\$A based systems: temperature and the partial pressures (abbreviated Pp) of the two reactive gas species, SO<sub>2</sub> and O<sub>2</sub>. In the simulations presented here, the gas phase is set in excess compared to the solid phase to maintain a constant partial pressure at all temperatures and achieve isobaric phase equilibria even though the solid phases may liberate or combine with gaseous species. This is a valid assumption for traditional cement manufacturing because of the continuous nature of rotary kiln operation where the atmosphere is renewed rapidly. For each phase diagram (see Figs. 1 and 2), the stable phases of a lime, silica, and alumina mixture suitable to produce one mole of alite and one mole of ye'elimite are determined via Gibb's free energy minimisation for a range of SO<sub>2</sub> partial pressures and temperatures. Aside from belite and calcium sulfate, all other phases such as rankinite (C<sub>3</sub>S<sub>2</sub>), mayenite (C<sub>12</sub>A<sub>7</sub>), and gehlenite (C<sub>2</sub>AS) are grouped together as C<sub>x</sub>A<sub>y</sub>S<sub>z</sub> for simplicity. The SO<sub>2</sub> and O<sub>2</sub> partial pressures reported are the initial atmospheric values, as at equilibrium they will partially combine to form SO<sub>3</sub> in the gas phase. Of the three main variables (temperature and partial pressure of SO<sub>2</sub> and O<sub>2</sub>), oxygen partial pressure is only evaluated at 1% and 5% for two reasons: (i) for simplicity, allowing presentation as a 2D diagram and (ii) conditions have to be maintained on the oxidative side of neutral to avoid sulfide formation in the kiln and the generation of sulphide solids and discharge of noxious sulfur containing gas species such as H<sub>2</sub>S. Thus, variations in O<sub>2</sub> partial pressure, are in practice, restricted to a narrow range of values when compared to numerical values for SO<sub>2</sub>. The thermodynamic data used in this work for C<sub>12</sub>A<sub>7</sub> was extrapolated beyond its 1427 °C upper limit using a linear C<sub>p</sub> temperature dependence assumption as liquid data is not yet available for this phase. The melting points of assemblages with C<sub>12</sub>A<sub>7</sub> are in the range 1400°C-1450°C. As only limited melt phase data is available (e.g., liquid C \$) and effects of mixing in the melt phase are ignored, the higher temperature results should be treated with caution; however, the trends still give valuable insight on the process limitations of simultaneous ye'elimite-alite production.

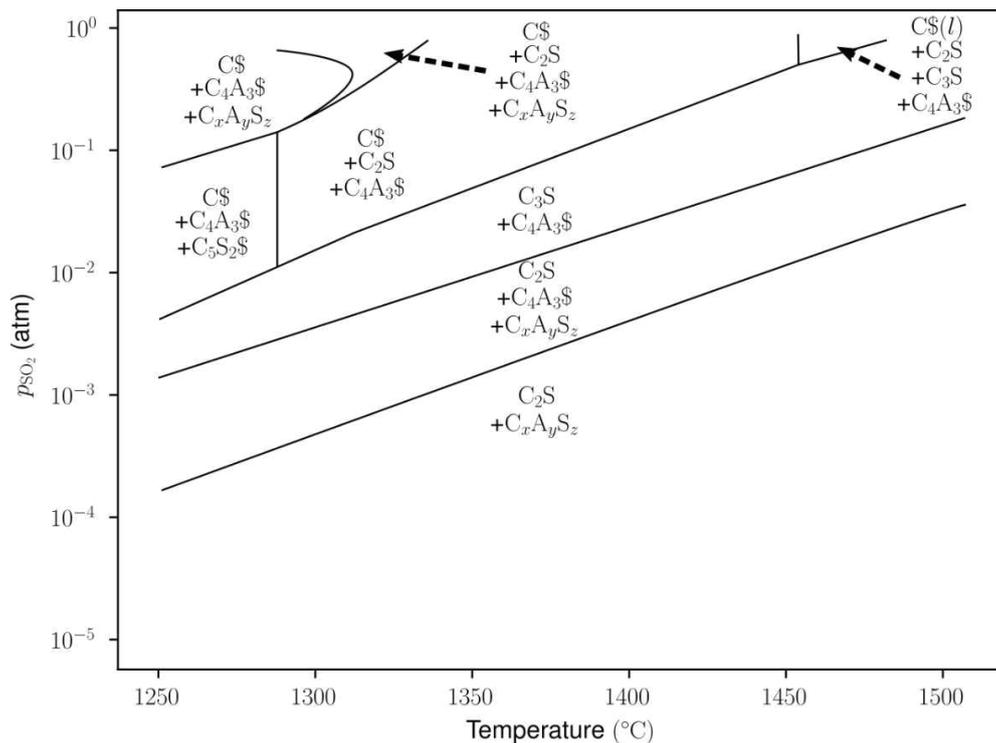
### 3.2 Thermodynamic boundaries for simultaneous a -C\$A clinker manufacture

Two energetic boundaries for the formation of a-C\$A clinker are identified (see Fig. 1 or 2). The first boundary is where the formation of alite and/or ye'elimite is inhibited as calcium increasingly combines with sulfur forming calcium sulfate. For example, in the C-S system, as temperatures increase and partial pressures of SO<sub>2</sub> and O<sub>2</sub> decrease, the general trend observed is:



The second boundary is observed where:  $\text{C}_3\text{S} + \text{C}_4\text{A}_3\$ = \text{C}_x\text{A}_y\text{S}_z + \text{C}_4\text{A}_3\$ + \text{C}_2\text{S}$ . As temperature increases, progressively higher SO<sub>2</sub> and O<sub>2</sub> pressures are necessary to maintain the stable coexistence of ye'elimite and alite.

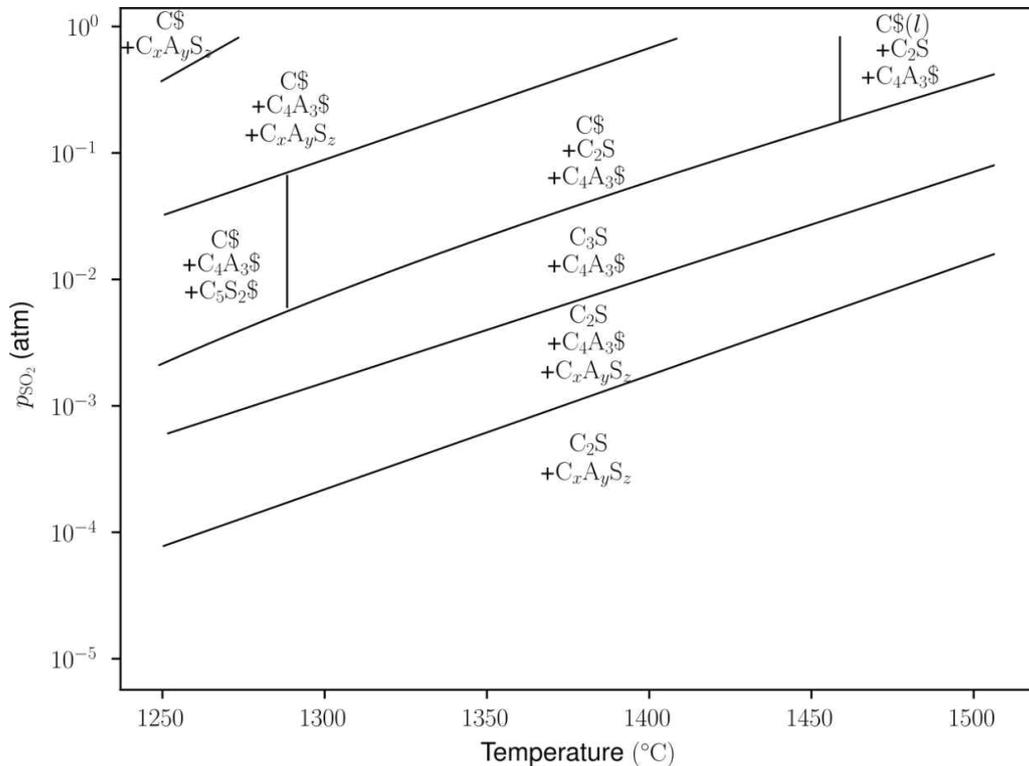
It is favourable that the process runs under oxidizing conditions for sulfur, i.e., the SO<sub>2</sub> Pp is less than two times the oxygen Pp. This condition is necessary to maintain an oxidizing environment and for SO<sub>2</sub> and O<sub>2</sub> to combine as "clinker SO<sub>3</sub>" or to be scrubbed from flue gas as SO<sub>3</sub>. As shown in Fig.1, an O<sub>2</sub> pressure of 1%v is not recommended for the co-formation of alite and ye'elimite. Although alite is thermodynamically stable above 1250 °C, it is not easily formed from conventional raw materials until temperatures greater than 1400 °C; thus, drawing a limit at ~2% SO<sub>2</sub> Pp, it can be observed that the operating zone is not satisfactory as the upper temperature limit of simultaneous alite and ye'elimite stability is below 1400°C and it is evident that a higher O<sub>2</sub> partial pressure is favourable.



**Figure 1: Phase diagram showing the region of stability for a-C\$A clinkers at various temperatures and SO<sub>2</sub> partial pressures where the initial O<sub>2</sub> partial pressure is 1%v. The total pressure is set at 1bar. N.B. melting will occur above ≈1350-1400°C; thus, the region above these temperatures must be evaluated carefully.**

The companion calculation but with an O<sub>2</sub> pressure set at 5%v is presented in Fig.2. The calculated diagram reveals that at 5% by volume O<sub>2</sub> coupled with an SO<sub>2</sub> partial pressure ranging from ≈3-10%v, the conditions for coexistence of alite and ye'elimite is extended to higher temperatures. The solidus

temperatures are not known but almost certainly, the pair ye'elimite-alite will be stable at the solidus so sintering in the presence of a reactive melt could facilitate the approach to equilibrium.



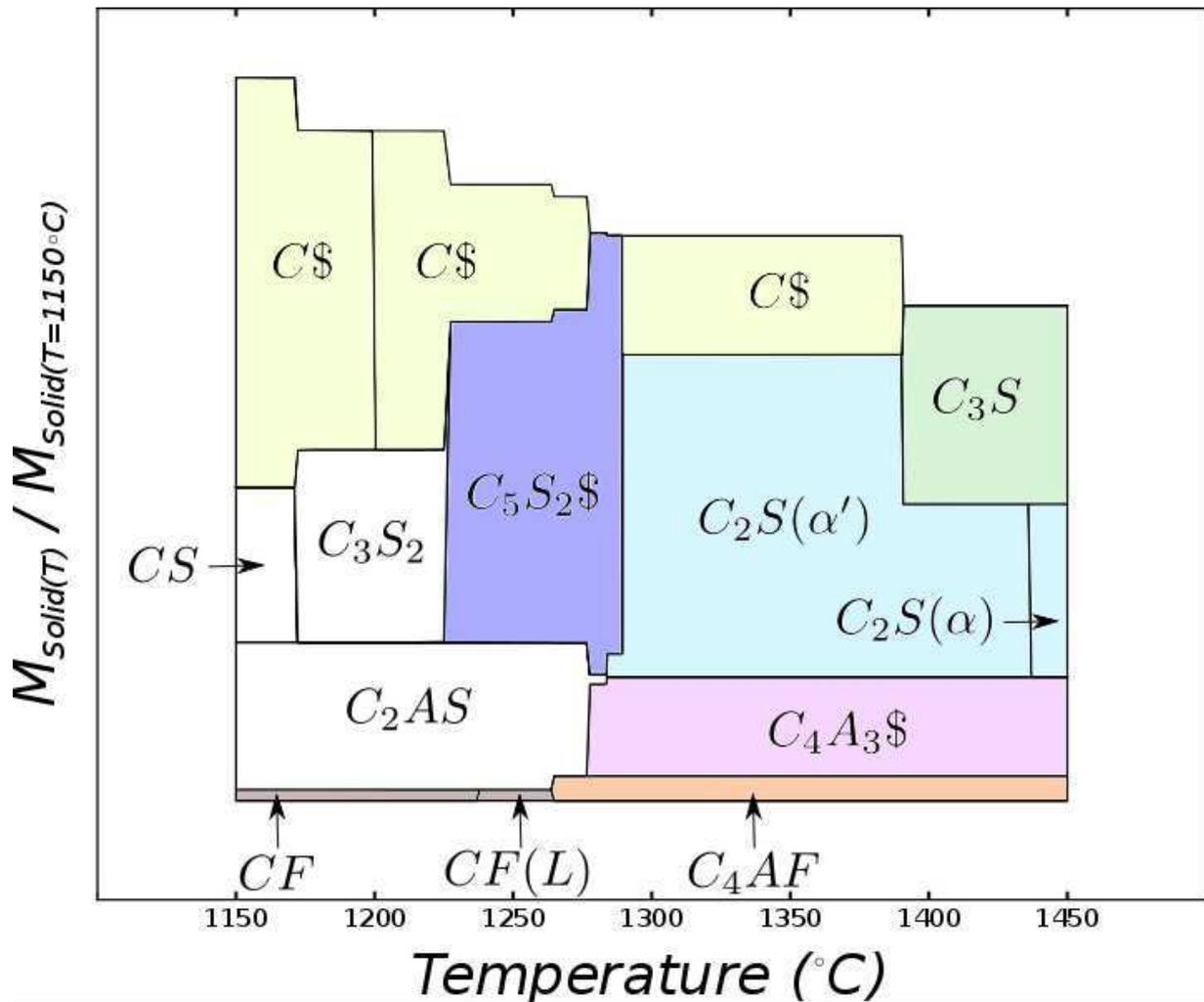
**Figure 2: Phase diagram showing the region of stability for a-C\$A clinkers at various temperatures and SO<sub>2</sub> partial pressures where the O<sub>2</sub> partial pressure is set constant at 5%v. The total pressure is set at 1bar. N.B. melting will occur above ≈1350-1400°C; thus, the region above these temperatures must be evaluated carefully.**

### 3.3 Phase evolution during a-C\$A clinkering under higher SO<sub>2</sub> and O<sub>2</sub> pressures

The solid phase evolution over clinkering zone temperatures has been evaluated at one atm total pressure. The SO<sub>2</sub> and O<sub>2</sub> pressures were each set at 5%v while the CO<sub>2</sub> pressure was set at 12%v to simulate the kiln combustion atmosphere and the remainder of the atmosphere was assumed to be nitrogen. The input solids are simple oxides of calcium, iron, aluminium, and silicon and are calculated such as to produce a final stoichiometric clinker assemblage of, by weight: 40% C<sub>3</sub>S, 35% C<sub>2</sub>S, 20% C<sub>4</sub>A<sub>3</sub>\$, and 5% C<sub>4</sub>AF. The solid input by weight is: 63.60% CaO, 23.34% SiO<sub>2</sub>, 11.37% Al<sub>2</sub>O<sub>3</sub>, and 1.69% Fe<sub>2</sub>O<sub>3</sub>. The sulfur component is assumed to be delivered to the clinker via the gas phase and, for simplicity, no alkali, titanium, or magnesium is included. The clinker phases at equilibrium for the temperature range 1150 – 1450°C are calculated and presented in Fig.3. Calculations were performed at 2°C intervals. Equilibrium is assumed at each step although it is accepted that, in practice, kinetic factors and low free energy driving forces near transition temperatures will produce departures from equilibrium; particularly at low temperatures.

Fig. 3 shows how the target clinker is produced during a single stage clinkering process. Two events, which do not normally occur during traditional cement manufacture, stand out in the clinker phase evolution diagram. The first is the formation of ternesite (C<sub>5</sub>S<sub>2</sub>\$) during the intermediate stage of clinkering at temperatures ranging from approx. 1220-1290°C; with the latter temperature being the

highest calculated temperature at which stoichiometric ternesite is stable under any gas fugacity (Hanein, Galan et al. 2017). Some studies have demonstrated that ternesite can exhibit cementitious properties (Sherman, Beretka et al. 1995, Dienemann, Schmitt et al. 2013, Bullerjahn, Schmitt et al. 2014, Bullerjahn, Zajac et al. 2015, Skalamprinos, Jen et al. 2018); however, if the formation of ternesite is unwanted, and there are chances of some ternesite formed during the intermediate stage persisting to the final clinker, its formation can be avoided by controlling temperature and  $\text{SO}_2$  and/or  $\text{O}_2$  partial pressures (Galan, Hanein et al. 2017, Hanein, Galan et al. 2017).



**Figure 3: The collective mass distribution of phases at equilibrium relative to the solid mass at 1150°C, evaluated for alite calcium sulfoaluminate clinker manufacture through atmospheric control, over the clinkering temperature range. The atmospheric conditions set are 5%v  $\text{SO}_2$  and 5%v  $\text{O}_2$ . The calculations are performed at intervals of 2°C. The line dividing the calcium sulfate at approx. 1200°C shows the polymorphic phase transition in C\$. N.B. melting will occur above  $\approx 1350\text{--}1400^\circ\text{C}$ ; thus, the region above these temperatures must be evaluated carefully.**

Another feature is the stability of calcium sulfate to very high temperatures; this is due to the higher  $\text{SO}_2$  and  $\text{O}_2$  pressures required to ensure ye'elite stability at higher temperatures. However, the most notable feature of the predicted diagram is the stability at high temperatures of the assemblage alite-belite-ye'elemite-ferrite. Although the calculations are extended to high temperatures it is

believed that extensive melting will occur above  $\approx 1350\text{-}1400^\circ\text{C}$ : experimental data are needed to include melting in the high temperature portion of Fig. 3.

### 3.4 Additional discussion

Recent pilot kiln trials (Hanein, Galan et al. 2016, Hanein, Galan et al. 2017) for C\$A based clinkers showed that both melt and ferrite are less evident amongst C\$A clinker produced in  $\text{SO}_2$  containing atmospheres than in conventional kiln atmospheres. However, in a-C\$A systems, promoted by the high alumina content, a melt phase will form at the higher clinkering temperatures that are necessary to form alite. This melt phase is probably also rich in iron oxide but cannot be captured by the model in its current configuration; thermodynamic data for the melt phase/solid solutions are required in order to accurately simulate the higher clinkering temperature zone.

Due to the lack of data for ion substitutions in all the phases associated with the manufacture of a-C\$A clinkers, another aspect not taken into account in this study is the aspect of sulfur uptake in belite such as that discussed by Herfort et al. (Herfort, Moir et al. 2010). However, future works should focus on determining the free energies of mineralised alite and belite.

Sulfur uptake into belite might also promote its reactivity in the course of subsequent hydration as sulfur substitution, in conjunction with other impurities could enable stabilisation of the alpha prime polymorph of belite to ambient (Elhoweris, Galan et al. 2018) which has been shown to be more reactive than the conventional beta polymorph (Cuberos, Ángeles et al. 2009).

## 4. The effect of iron and its role as a flux and/or mineraliser during a-C\$A clinker production

### 4.1. Background

Odler and Zhang (Odler and Zhang 1996, Zhang and Odler 1996) investigated high  $\text{SO}_3$  containing Portland clinkers made with the addition of  $\text{CaF}_2$ . To attain high compressive strength binders, they targeted a clinker containing 70 wt.%  $\text{C}_3\text{S}$  and 30 wt.%  $\text{C}_4\text{A}_3\text{S}$  at  $1300^\circ\text{C}$ . No quantitative analyses are included in their study; however, the introduction of  $\text{Fe}_2\text{O}_3$ ,  $\text{CaF}_2$ , and calcium sulfate was reported to decrease the clinkering temperature. The production of (70%  $\text{C}_3\text{S}$  + 20%  $\text{C}_4\text{AF}$  and 10%  $\text{C}_4\text{A}_3\text{S}$ ) and (70%  $\text{C}_3\text{S}$  + 10%  $\text{C}_4\text{AF}$  and 20%  $\text{C}_4\text{A}_3\text{S}$ ) clinkers was achieved at  $1250^\circ\text{C}$  and  $1230^\circ\text{C}$ , respectively, and complete reaction validated through the low free lime contents, determined to be 0.24 and 0.53%, respectively, compared to 0.51% for the 70%  $\text{C}_3\text{S}$  and 30%  $\text{C}_4\text{A}_3\text{S}$  clinker fired at  $1300^\circ\text{C}$ . More recent results obtained in the CAER laboratory at the University of Kentucky demonstrated that melting temperatures of mixtures of fluorellestadite and ferrite varied depending on their proportions. Five different mixtures with various ratios of fluorellestadite and ferrite were produced following the formulations presented in Tab.2. Each of these formulations was tested through differential thermal analysis (DTA), performed in a Netzsch STA 449, under air atmosphere at 100 mL/min, with alumina open pans, from room temperature to  $1400^\circ\text{C}$ ; the results are shown in Tab.3 and Appendix 1. The se results showed that the sample containing ferrite, on its own, starts to melt at  $1382^\circ\text{C}$ , while the melting of fluorellestadite starts at  $1245^\circ\text{C}$ . Measurements of the melting temperature through DTA of mixtures of fluorellestadite and ferrite at weight ratios of 1:2, 1:1, and 2:1 revealed that they interact with each other and decrease the melting temperature.

**Table 2: Formulations of mixtures of fluorellestadite and ferrite in weight percentages.**

Ratio of $3\text{C}_2\text{S}.3\text{CaSO}_4.\text{CaF}_2$ and $\text{C}_4\text{AF}$	$\text{Ca}(\text{OH})_2$	$\text{SiO}_2$	$\text{Al}(\text{OH})_3$	$\text{Fe}_2\text{O}_3$	$\text{CaSO}_4.0.5\text{H}_2\text{O}$	$\text{CaF}_2$
0:1	48.42	-	25.49	26.09	-	-
1:2	43.91	7.63	13.21	13.52	18.43	3.30
1:1	42.33	10.30	8.91	9.12	24.88	4.46
2:1	41.04	12.48	5.40	5.53	30.15	5.41
1:0	39.05	15.84	-	-	38.25	6.86

**Table 3: Melting temperatures from DTA analyses of mixtures of fluorellestadite and ferrite.**

$3\text{C}_2\text{S}.3\text{C}_4\text{AF} : \text{C}_4\text{AF}$	First melting event (°C)	Second melting event (°C)
0:1	1382	-
1:2	1193	1306
1:1	1204	1292
2:1	1208	1269
1:0	1245	-

These results indicate that both fluorellestadite and ferrite may act as mineralizers and fluxes for the synthesis of a-C\$A clinkers and that intermediate phases may form. Here, preliminary work has been carried out to study the influence of both  $\text{CaF}_2$  and  $\text{Fe}_2\text{O}_3$  addition in the synthesis of a-C\$A clinkers.

#### 4.2. Materials and Methods

The reagent grade chemicals listed in Tab.4 were used for the preparation of clinkers. Four batches were targeted for production, designated A-CSA #1, 2, 3, and 4. The aim was to produce clinker mineralogy comprising approximately 50:50 by weight alite and ye'elimite, as presented in Tab. 5 in more details. The theoretical clinker compositions were calculated using modified Bogue equations, as described previously (Duvallet 2014, Duvallet, Zhou et al. 2015). The four batch compositions are presented in Tab.5 along with the calculated clinker phase assemblage. In the first batch, A-CSA #1, no extrinsic mineralizers or fluxes were added. Enough calcium fluoride, to produce 10% by weight fluorellestadite was added to A-CSA #2. A-CSA #3 contains enough iron to produce 5% by weight  $\text{C}_4\text{AF}$ , while A-CSA #4 contains both iron and  $\text{CaF}_2$ .

**Table 4: Information on chemicals used in this work for a-C\$A clinker syntheses.**

Compound	Formula	Purity	Particle size	Supplier
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	98+%	NA	Acros Organics
Silicon dioxide	$\text{SiO}_2$	99.6% metal basis	-325 mesh	Aldrich Chemistry
Aluminium hydroxide	$\text{Al}(\text{OH})_3$	Extra pure	Powder	Acros Organics
Iron (III) oxide	$\text{Fe}_2\text{O}_3$	>99%	<5 micron	Sigma-Aldrich
Calcium sulfate hemihydrate	$\text{CaSO}_4.1/2\text{H}_2\text{O}$	97+%	NA	Acros Organics
Calcium fluoride	$\text{CaF}_2$	99.5+%	-325 mesh	Sigma-Aldrich

Disks of 28 x 7 mm were produced by mixing 10 g of raw materials with 10% by weight of deionised water and pressed under 25000 lbs pressure; the appearance of the disks are shown in Fig.4. The

disks were dried in an oven at 60°C overnight, and the samples were then placed in a platinum crucible and fired in a box furnace with the following program: 1) ramp from room temperature to 800°C at 7.5°C/min, 2) dwell at 800°C for 30 minutes, 3) ramp from 800°C to 1250°C at 5°C/min, 4) dwell at 1250°C for 60 minutes, and 5) quenched rapidly in air by removing samples from the furnace. The atmosphere inside the oven and kiln was not controlled but it is assumed to be similar to ambient.

**Table 5: Raw mix compositions and theoretical clinker assemblage of the four batches a-CSA with and without fluorellestadite and/or Fe<sub>2</sub>O<sub>3</sub>.**

ID	Reagent Chemicals (in wt.%)						Theoretical Clinker Compositions (in wt.%)					
	Ca(OH) <sub>2</sub>	SiO <sub>2</sub>	Al(OH) <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaSO <sub>4</sub> ·1/2H <sub>2</sub> O	CaF <sub>2</sub>	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>4</sub> A <sub>3</sub> S	C <sub>4</sub> AF	C\$	CaF <sub>2</sub>
A-CSA #1	51.54	9.86	29.6	-	9.0	-	48.5	-	49.9	-	-	-
A-CSA #2	51.235	9.815	29.4	-	8.95	0.6	48.0	0.1	49.5	-	-	0.78
A-CSA #3	50.89	9.21	29.6	1.3	9.0	-	45.0	0.1	47.7	5.0	0.5	-
A-CSA #4	50.57	9.13	29.5	1.3	8.895	0.605	44.7	-	47.4	5.0	0.4	0.78



**Figure 4: Image of the four 28x7 disks of A-CSA #1-4 before being fired in a platinum crucible, with A-CSA #1 located at the bottom left of the image, followed by A-CSA #2, #3, and #4 towards top right. A-CSA #3 and #4 are red due to the presence of iron.**

The clinker phase assemblage was then determined by X-ray diffraction and quantified using the Rietveld refinement method successfully used in previous studies to determine the influence of mineralizers and/or fluxes in clinkers (Blanco-Varela, Palomo et al. 1984, Xu and Lou 1993, Dominguez, Torres-Castillo et al. 2010, Snellings, Schepper et al. 2012). Diffraction patterns were collected with a Philips X'Pert diffractometer (PW3040-PRO X'Pert) in the Bragg-Brentano geometry armed with a Cu K- $\alpha$  radiation source operated at 45 kV and 40 mA. The samples were ground by hand in a ceramic mortar and pestle, dry mounted in aluminium holders, and scanned from 8-90° 2 $\theta$ . The analyses software used was HighScore Plus from Panalytical™.

To determine melting temperatures, each raw mix batch was analysed using simultaneous thermal analyses: thermogravimetry and differential scanning calorimetry. Approximately 20-40 mg of sample was placed in an alumina open pan, and was measured on a TA instruments SDT Q600 from 50 - 1400°C at a heating rate of 10°C/min under an air atmosphere flowing at 100 mL/min.

### 4.3. Results

Quantitative phase analysis measurements are presented in Tab.6. Sample A-CSA #1, with no supplementary mineralizers or fluxes, did not form a significant quantity of alite but instead showed the formation of 46 wt.% belite, and 41 wt.% calcium sulfoaluminate. The free lime was high, at 8.4 wt.%, due to incomplete reaction. The addition of calcium fluoride in A-CSA #2 promoted the formation of alite, (13.4 wt.%); although, 5.6 wt.% free lime remained. The addition of  $\text{Fe}_2\text{O}_3$  in A-CSA #3 promoted the formation of alite compared to A-CSA #1, but not compared to A-CSA #2 (containing fluorine). However, in A-CSA #4, the presence of both fluorellestadite and  $\text{Fe}_2\text{O}_3$  enhanced the formation of alite, at 24.5% by weight; this is almost double that in A-CSA #2 (containing fluorine). In addition, the free lime content was very low, 2.8 wt.%. It can be noted that the measured mineralogical compositions are slightly different from the theoretical ones, especially for the alite content. Even if taking into account the presence of free lime, and assuming that the remaining free lime would react with belite to form alite, the overall alite content would reach 35 wt.% in all compositions with around 10-15 wt.% belite. This can be explained by the free lime reacting with alumina to form additional clinker phases, such as  $\text{C}_{11}\text{A}_7\text{CaF}_2$  and  $\text{C}_{12}\text{A}_7$  and thus not forming alite. Another explanation would be that the calcium hydroxide used as raw ingredient for the production of the compositions presented in Tab.6 may have included additional impurities, leading to a lack of free lime for the formation of alite. Either way, these data prove that the combination of  $\text{CaF}_2$  and  $\text{Fe}_2\text{O}_3$  act as mineralizers and/or fluxes for the formation of alite-C\$A clinkers.

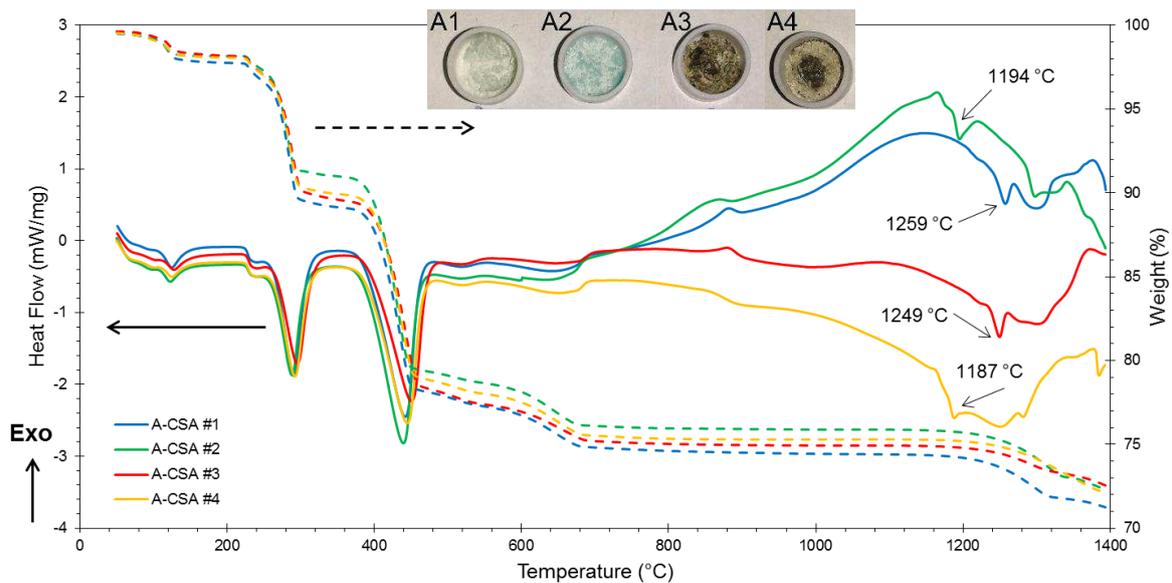
Simultaneous thermal analyses were then performed to determine the melting temperatures of the compositions listed in Tab.5; results are presented in Fig.6. The first three sets of peaks observed for all compositions at around 100°C, 300°C, and 450°C correspond to the loss of free water, the decomposition of aluminium hydroxide, and the decomposition of calcium hydroxide, respectively (confirmed by weight loss from thermogravimetry). Compositions A-CSA #1 (with no mineralizers/fluxes added) and A-CSA #3 (with only  $\text{Fe}_2\text{O}_3$  added) showed endothermic melting events at 1259°C and 1249°C, respectively. The addition of  $\text{Fe}_2\text{O}_3$  did not seem to decrease the melting temperature of the a-C\$A formulation, even though some alite formed, as determined by Rietveld analysis. On the other hand, the melting temperatures of A-CSA #2 and A-CSA #4 were very similar: 1194°C and 1187°C. It is observed that the addition of both  $\text{CaF}_2$  and  $\text{Fe}_2\text{O}_3$  to the a-C\$A clinker did not contribute significantly to reducing the melting temperature (reduced by only 7°C), but it did significantly enhance the formation of alite in the clinker composition. As shown in Tab.6, alite increasing from almost zero in A-CSA #1, to  $\approx 13\%$  by weight in A-CSA #2, and  $\approx 25\%$  in A-CSA #4. It can be observed in Fig.5 that the baselines for all samples shift; this may be attributed to changes in the sample weights as the baselines start to shift following a weight loss, at around 600-700 °C. In addition, images of the samples following the thermal analyses are also included in Fig.6. A-CSA #1 was white, while A-CSA #2 with only  $\text{CaF}_2$  as additives is light blue. A-CSA#3 and A-CSA #4 are both dark brown due to the presence of iron.

These preliminary results demonstrate that both compounds together, fluorine and iron, significantly influence the formation of a-C\$A clinker at 1250 °C, by enhancing the formation of alite.

**Table 6: Quantitative phase analyses of samples A-CSA #1-4 measured via the Rietveld method in weight percentages, with the ICDD files numbers, and the Rietveld parameters. N.B. FI\* = fluorellestadite; Rexp = Expected R Factor; Rp = Residual of Least-Squares Refinement; Rwp = Weighted Profile R-Factor; GoF = Goodness of Fit.**

			A-CSA #1	A-CSA #2	A-CSA #3	A-CSA #4
Expected Compositions	C <sub>3</sub> S		48.5	48.0	45	44.7
	C <sub>2</sub> S		0	0.1	0.1	0
	C <sub>4</sub> A <sub>3</sub> \$		49.9	49.5	47.7	47.4
	C <sub>4</sub> AF		0	0	5.0	5.0
	C\$		0	0	0.5	0.4
Mineralizers/Fluxes present		Ref.	Nothing	FI*	Fe <sub>2</sub> O <sub>3</sub>	FI* & Fe <sub>2</sub> O <sub>3</sub>
Rietveld calculations	C <sub>3</sub> S	(de Noirfontaine, Dunstetter et al. 2006)	0.5	12.4	3.8	24.4
	C <sub>2</sub> S-Beta	(Mumme, Hill et al. 1995)	44.5	33.0	40.4	22.0
	C <sub>2</sub> S-Low Alpha	(Mumme and Cranswick 1996)	-	-	1.1	-
	C <sub>4</sub> A <sub>3</sub> \$* (orthorhombic)	(Calos, Kennard et al. 1995, Cuesta, De la Torre et al. 2013)	40.7	42.5	38.7	41.5
	C <sub>4</sub> AF	(Colville and Geller 1971)	1.4	1.0	4.5	3.7
	C\$	(Kirfel and Will 1980)	0.3	0.0	0.2	0.2
	C (Free Lime)	(Panalytical and Diffraktometer 2011)	9.2	5.7	8.3	3.0
	M (MgO)	(Panalytical and Diffraktometer 2011)	0.3	0.2	0.3	0.1
	C <sub>12</sub> A <sub>7</sub>	(Boysen, Lerch et al. 2007)	-	0.1	0.8	2.9
	CA	(Horkner and Mullerbuschbaum 1976)	1.0	0.2	0.5	0.3
	C <sub>3</sub> A	(Mondal and Jeffery 1975)	-	-	-	-
	C <sub>11</sub> A <sub>7</sub> CaF <sub>2</sub>	(Costa and Ballirano 2000)	2.1	4.7	1.4	1.8
	FI*	(Pajares, De la Torre et al. 2002)	-	-	-	-
Rietveld Parameters	Rexp		2.39	2.36	2.24	2.23
	Rp		5.69	5.47	4.50	4.75
	Rwp		8.56	8.37	6.69	7.02
	GoF		3.58	3.55	2.98	3.15

\* Rietveld analyses is performed using the crystal structure of ye'elimite presented in Cuesta et al. 2013 but with the thermal parameters from Calos et al. 1995.



**Figure 5: Heat flow and weight loss results for compositions presented in Tab. 5 and 6, performed with a TA Instrument SDT Q600, from 50 to 1400 °C, in Air (100 mL/min). Images of the samples following the thermal analyses are also presented (inset).**

## 6. Conclusions

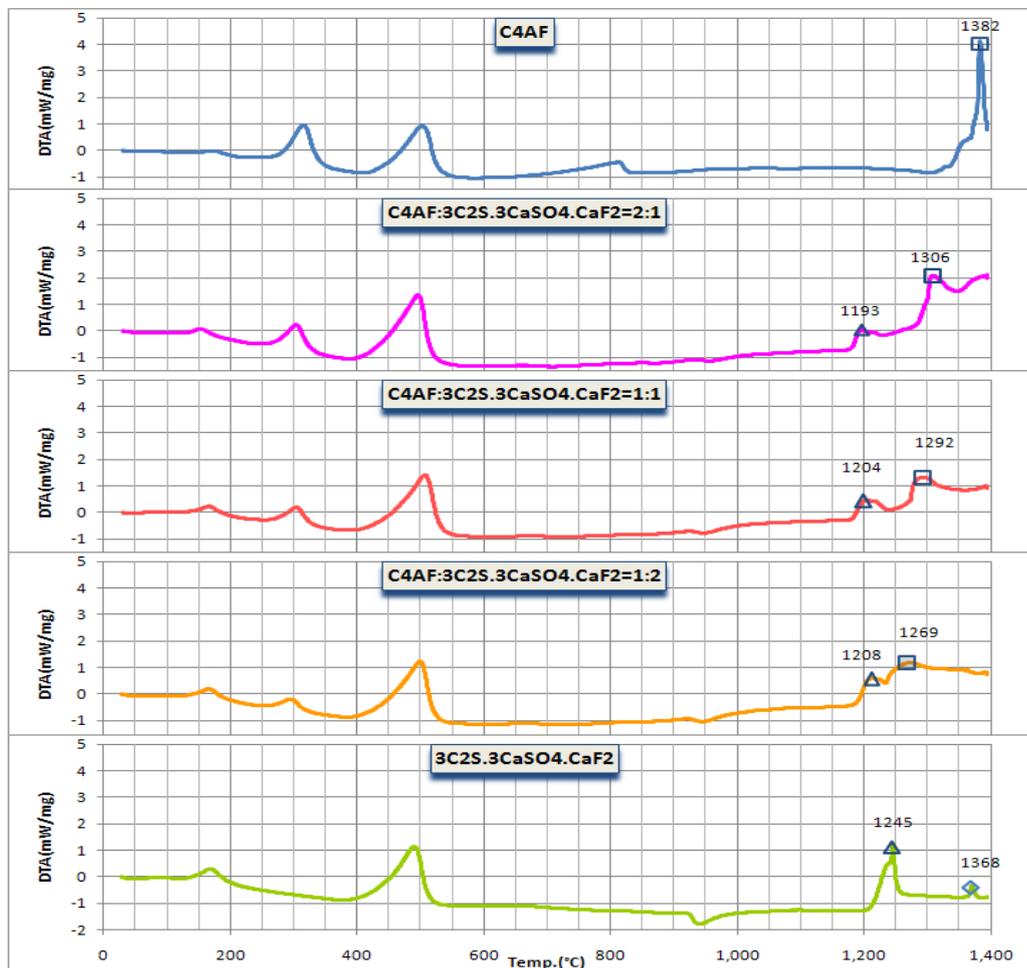
Two novel approaches for the manufacture of a-C\$A clinker have been identified; however, both routes remain to be explored with respect to the hydration characteristics of the clinker. The first route, resulting from a thermodynamic study, shows how control of the process atmosphere can be used to stabilise ye'elimite to higher temperature allowing for the coexistence and simultaneous formation of alite and ye'elimite; mineralisers are not needed. The necessary "SO<sub>3</sub>" can be added to the raw meal, or supplied via the combustion atmosphere, or both.

The second approach uses a flux/mineraliser combination consisting of CaF<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> to improve reaction efficiency; however, the exact mechanisms behind this second approach are still unknown but the presence of melt at clinkering temperatures seems critical and also, from previous studies (Shame and Glasser 1987), alite stability is enhanced with respect to mixtures of mainly lime and belite by the simultaneous partial replacement of silicon by aluminium and of oxygen by fluorine. Further work is required in order to optimise clinkering temperatures and the iron, fluorine, and sulfate content of the raw mix. This approach also shows potential for the re-use of wastes from the metal industry such as slags which contain fluorine and iron; and, which are also a source of already-decarbonised CaO that will contribute to reducing further the carbon footprint of a-C\$A cement manufacture. It is well known that fluorine addition affects the setting time in PC; thus, mineralisation with fluorine to produce a-C\$A clinker may also influence the properties of the resulting cement. Therefore, the performance of these cements will also need to be tested.

This work also proves that thermodynamic studies can speed-up the development and understanding of clinkering in novel systems and that the coupling of thermodynamic modelling with experiment is necessary. However, thermodynamic models/data including the melt phase and solid solutions in C\$A-based systems are scarce and further work is required to develop these models in order to completely simulate the production of potential future cements. Nevertheless, empirical methods alone have failed to realise the potential of cements and even the small amount of work done thus far

on improved models has revealed that new and exciting possibilities emerge for improving the engineering properties of cement and lowering the CO<sub>2</sub> footprint of construction.

## 7. Appendix



**Appendix 1: Comparison of DTA analyses of the different compositions of ferrite and fluorellestadite.**

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