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Advances in clinkering technology of calcium sulfoaluminate cement

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According to your comments, better quality images have now been added and the format of the manuscript has been revised.

Advances in clinkering technology of calcium sulfoaluminate cement

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Abstract

A new method for producing calcium sulfoaluminate ($C\bar{S}A$) clinkers is described. Sulfur is introduced from the gas phase as SO_2 and oxygen and reacts with solids during clinkerisation. Laboratory experiments and thermodynamic calculations are presented. Sulfur-containing phases, ye'elimite and ternesite, are stabilised together with belite to produce clinkers with various mineralogies. The influence of temperature and SO_2 partial pressure is analysed and their effect on the formation of undesirable anhydrite and gehlenite is explained. The process by which a potentially hazardous waste material such as sulfur is used as raw material, and possibly as fuel, to form $C\bar{S}A$ cements, is shown to be successful.

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Clinkering/clinkering reactions; Diffraction (X-ray); Mineralogy; Modelling; Special cements; Thermodynamics; Waste valorisation

List of notation

C	CaO
S	SiO_2
A	Al_2O_3
$\bar{S}$	SO_3
F	Fe_2O_3

1. Introduction

The formulation of calcium sulfoaluminate ($C\bar{S}A$) cements is undergoing rapid development as a prelude to widespread application. The advantages of $C\bar{S}A$ cements relative to ordinary Portland cement (OPC) have been reported (Gartner 2004, Hanein et al. 2016, Gartner, Hirao 2015, Gartner, MacPhee 2011, Juenger et al. 2011) and include reduction of CO_2 emissions and lower specific energy requirements.

The major benefits of $C\bar{S}A$ cements primarily arise due to the presence of abundant ye'elimite ($C_4A_3\bar{S}$) giving, among other advantages, high early strength. But other sulfur containing phases, including ternesite ($C_5S_2\bar{S}$) and anhydrite ($C\bar{S}$) can occur. $C\bar{S}A$ clinkers require a source of sulfur trioxide, commonly provided by addition of anhydrite to the clinker or either active anhydrite or gypsum to the raw mix. However, the formation of $C\bar{S}A$ clinker is challenging, particularly under laboratory conditions, due to volatilisation of SO_3 (the stable gas phase lost at elevated temperatures is in fact a mixture of SO_2 and O_2 from the solids) or, more generally, the inability to stabilise the clinker SO_3 content.

At clinkering temperatures, typically >1250 °C but lower than melting temperatures, which occur at >1300 °C (Idrissi et al. 2010, Touzo, Scrivener & Glasser 2013), the loss of SO_3 limits clinkering to a rather narrow window of temperatures and requires that the exhaust gas from the kiln is monitored and, if necessary, scrubbed to remove SO_x. The present paper shows that this loss need not be a problem, particularly on an industrial scale: the high pressures of sulfur oxides can be used to an advantage and vapour transport is shown to be an effective way of achieving reaction amongst the components of the raw meal. Kinetic studies show that the equilibrium between gas and solid components is achieved rapidly at ≈1300 °C, even in the rapid flow rates achieved in commercial kilns.

Most experience of clinkering has been gained by laboratory experiments supplemented by pilot plant "burns". In the present study, a somewhat different approach was taken. Experiments and thermodynamic calculations were combined to elucidate the clinkering process. The work demonstrates the importance of the vapour phase to clinkering and has led to changes in kiln operation: the kiln is modified to work as a semi-sealed system in order to gain control of the kiln atmosphere. This has been paralleled by using a small capacity (10-100g) laboratory kiln

permitting independent control of temperature and gas partial pressures of SO_2 and O_2 and total pressure 1 bar.

Numerous high temperature thermodynamic equilibrium models based on Gibbs energy minimization have been developed for cement clinker predictions and have proved useful in cement research (Barry, Glasser 2000, Hökfors et al. 2015, Hökfors, Eriksson & Viggh 2014). Thermodynamic databases used to calculate high temperature cement phase equilibria include, MTDATA (Davies et al. 2002), FactSage (Bale et al. 2002), HSC (Roine 2002) and that recently developed by Hanein et al. (Hanein, Glasser & Bannerman 2015). As shown by Hanein et al. (Hanein et al. 2015), the stability of ye'elimite at clinkering temperatures is dependent on the fugacities (which we equate with partial pressures) of both SO_2 and O_2 in the kiln atmosphere and a thermodynamic model considering both the clinker phases and atmosphere has been developed to model the reaction path and optimising operating conditions for the production of $C\bar{S}A$ clinkers.

2. Experimental

2.1. Furnace

Experiments were conducted in a tube furnace specifically modified to operate at one bar total pressure but with controlled partial pressures of SO_2 and O_2 (Galan et al. 2014), see Figure 1. The pre-mixed gases, whose rates were monitored by means of precision mass flow controllers (Bronkhorst, NL), pass through the non-rotating furnace tube maintaining the desired atmosphere during the experiment. The discharge end of the tube is connected to a scrubber that absorbs and neutralizes unreacted SO_x prior to gas discharge to the atmosphere. In that way, exit gases achieve less that 1ppm SO_x. Temperature patterns (heating, idling and cooling) were programmed at the furnace control box.

2.2. Raw materials

Two sets of raw materials were used for the experiments:

Set 1: laboratory grades of Al_2O_3 (Sigma-Aldrich 265497, 10 μm, 99.7%), SiO_2 (quartz, Fluka 83340, >230 mesh, >95%), $CaCO_3$ (Sigma-Aldrich 795445, >99%), Fe_2O_3 (Fisher Scientific I/1150/53, general purpose grade) and $CaSO_4$ (Fisher C/2440/60, >95%).

Set 2: commercially available bauxite, clay and limestone. The oxide composition of the commercially available raw materials is shown in Table 1. The bauxite and the clay were provided by Zhengzhou Haixu abrasives Co. Ltd. (China), and the limestone was provided by Samin (France).

In both cases the raw materials were weighted, mixed, placed in crucibles or boats of aluminous porcelain or Pt, and introduced in the furnace which was ramped up to an isothermal level.

2.3. Experiments

The variables evaluated in the experiments described in this work include: SO_2 partial pressure, peak clinkering temperature, proportioning of raw materials and time. The O_2 partial pressure was kept sufficiently high to ensure oxidizing conditions to (i) prevent formation of undesirable sulfides and (ii) ensure all SO_2 is able to oxidize to SO_3 if the equilibrium sought demands formation of solids containing sulfate. The minimum O_2 excess was targeted at 100%, resulting in weight ratios SO_2:O_2 at least 1:0.5 (or SO_2:air, 1:2.5).

Approximately 25 compositions were tested and in all cases the atmosphere conditions were such that SO_3 was transferred from the vapour to the solid to achieve the target mineralogy. This was achieved providing an automatic check that the kinetics of transfer of sulfur species from gas to solid are rapid. The experiments included: (i) formation of $CaSO_4$ by transfer of SO_2+O_2 from the vapour to powdered $CaCO_3$ or CaO, (ii) formation of ye'elimite ($C_4A_3\bar{S}$) and ternesite ($C_5S_2\bar{S}$) by transfer of SO_2+O_2 to appropriate mixes of CaO and Al_2O_3, and CaO and SiO_2, respectively, and (iii) clinkers designed to contain $C_4A_3\bar{S}$, belite (C_2S) and ferrite (solid solution C_2F-C_6A_2F) by transfer of SO_2+O_2 to mixes of CaO, Al_2O_3, SiO_2 and Fe_2O_3. The different compositions were prepared by hand mixing the calculated amounts of dry solid reactants using a mortar and a pestle with a few drops of ethanol added to aid homogenisation, for 5 minutes. The resulting mix was dried in an oven at ≈100 °C for 2 hours to remove the alcohol. Clinkers were prepared from lab grade materials in the form of pellets (Table 2) and in powder (Table 3) and using commercially available raw materials (Table 4) in powder form with a particle size of approximately 40 microns. In experiments 1-11 in Table 3 lab grade calcium sulfate ($C\bar{S}$) was also added to the raw mix.

- Clinkers made with $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3. Three different mixes were prepared in the form of 13 mm diameter pressed pellets. These were fired at 1300 °C for 30 minutes. Targeted mineralogies and gas flow conditions are shown in Table 2. The amount of sulfur introduced in the furnace was in all cases sufficient to form the target amount of $C_4A_3\bar{S}$. The rate of SO_2 used allowed for the formation of a minimum of 1.5 grams of "SO_3" in the 30 minutes the gases were passing through the tube furnace. The quantities of SO_3 required to obtain the target compositions 1, 2 and 3 in Table 2 were 0.21, 0.13 and 0.05 grams, respectively. C_6A_2F was chosen as the target stoichiometry for ferrite based on trends shown by Touzo el al. (Touzo, Scrivener & Glasser 2013) for feeds with high Al_2O_3:Fe_2O_3 ratios, but changes were made in the course of the work because experiments showed that the actual ferrite lay close to C_4AF.

- Clinkers made with $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and $CaSO_4$. In this set of experiments the SO_2+O_2 was turned on when the furnace reached ≈600 °C during ramp up (at 20 °C/min) and turned off during the cooling cycle (at 20 °C/min) below ≈600 °C. To facilitate reaction between gas and solid phases, a layer of the solid reactants several mm thick, ≈10 grams in total, was placed in a 15 cm long ceramic boat in the middle of the hot zone of the tube (at constant temperature). The mix proportions used and the experimental conditions (SO_2:air ratios and temperature) are summarised in Table 3. The time allowed for reaction, ≈120 minutes, does not include ramping up and down times. The amount of $CaSO_4$ was in all cases enough to form the desired target compositions; the SO_2+O_2 atmosphere was used to preclude sulfur losses from the solids, and to keep an atmosphere with an excess of "SO_3" at all times.

- Clinkers made with commercially available raw materials. Two different mixes were used under two different conditions. The mixes used were calculated for a certain target composition assuming silica (from both the clay and bauxite) will form belite (C_2S), the iron oxide will combine with Ca and Al oxides to form ferrite (C_4AF) and the excess of Al oxide react to form ye'elimite ($C_4A_3\bar{S}$). The gas atmosphere was on from the beginning

to the end of the experiments (to prevent possible sulfur losses during ramping up and down). As in the lab grade experiments, a layer of the solid reactants several mm thick, ≈10 grams in total, was placed in a ceramic boat in the middle of the hot zone of the tube (at constant temperature). The proportions used and the experimental conditions (SO_2 partial pressure, temperature and time) are summarised in Table 4. In the column 'time' the number indicates the actual time at peak temperature. The excess of SO_3 in these cases was higher: the mass of SO_3 that would pass through the tube during the time at peak temperature (around 6 g) was 3-4 times higher than the amount needed in theory for the target mineralogies (around 2.2 g and 1.4 g, respectively). For these experiments C_4AF was chosen as the target stoichiometry for ferrite, as opposed to the C_6A_2F used for the previous ones. This was done for several reasons: the exact stoichiometry for ferrite in $C\bar{S}A$ mixes is not well known and both extremes of the solid solution had to be checked; also, according to the results, the ferrite phase made in SO_2+O_2 atmospheres seems to be variable, but both the standard used for Rietveld refinement and the data for the thermodynamic modelling consider C_4AF.

2.4. Characterisation

The products obtained were characterised by X-ray powder diffraction using an Empyrean diffractometer (PANalytical) with strictly monochromatic CuKα1 radiation (λ = 1.54056 Å) at 45 kV and 40 mA. In order to determine the composition of the samples, they were analysed using the Rietveld methodology as implemented in the GSAS software package (Larson, Von Dreele 2004). Final global optimised parameters included background coefficients, zero-shift error, cell parameters and peak shape parameters. Peak shapes were fitted using the pseudo-Voigt function (Thompson, Cox & Hastings 1987) with an asymmetry correction included (Finger, Cox & Jephcoat 1994). A March-Dollase ellipsoidal preferred orientation correction algorithm (Dollase 1986) was used when preferred orientation parameter needed refinement. The crystal structure descriptions for the different phases encountered were: (Cuesta et al. 2013) for orthorhombic ye'elimite, (Cuesta et al. 2014) for cubic ye'elimite, (Mumme et al. 1995) for β-belite, (Colville, Geller 1971) for ferrite, (Louisnathan 1971) for gehlenite, (Irran, Tillmanns &

Hentschel 1997) for ternesite, (Hörkner, Müller-Buschbaum 1976) for calcium monoaluminate, (Kirfel, Will 1980) for anhydrite and (Sasaki et al. 1987) for perovskite.

2.5. Thermodynamic modelling

A thermodynamic model based on Gibbs energy minimisation and a recently compiled high temperature cement clinker stoichiometric phase thermodynamic database (Hanein, Glasser & Bannerman 2015) was used to supplement the experimental data: raw mix input and experimental conditions included in Table 4 were 'replicated' for the model calculations. The thermodynamic data for ye'elimite and ternesite ($C_5S_2\bar{S}$) were recently derived by the authors (Hanein et al. 2015, Hanein et al. 2017). The thermodynamic model and compiled database used here have been validated in several studies (Hanein, Glasser & Bannerman 2015, Hanein et al. 2015, Hanein et al. 2017, Galan et al. 2017, Hanein et al. 2016). As a means of emulating the furnace operation (continuous counter-current flow) and to maintain constant SO_2 and O_2 partial pressures in the system, the gaseous atmosphere is assumed to be in excess (m_{gas}>> m_{solids}). P_2O_5 and MnO were neglected in thermodynamic simulations due to the lack of thermodynamic data for these species and phases containing them. The database also does not have thermodynamic data for C_6A_2F; C_4AF is the only calcium aluminoferrite for which data are currently available. The model used takes into account both the solids and the atmosphere surrounding them simultaneously. For comparison, only major phases formed and detected in XRD measurements of experimental runs are shown from the model results in Table 8. However, the model also accounts for all the species shown in Table 1 (except MnO and P_2O_5) and all the calculations carried out predict the conversion of all alkali to alkali sulfates; MgO also appears to remain unreacted in the thermodynamic calculations.

3. Results

3.1. Transfer of sulfur between gas and solids

The transfer of sulfur from gas to solid was confirmed to be rapid at 900-1000 °C and above: CaO reacted readily and completely with mixes of SO_2 and O_2 to form $CaSO_4$. For these experiments different flow rates and ratios SO_2:air were used (0.1:0.25, 0.434:1.058, 0.868:2.116 and 0.217:0.529 g/min), and they were performed using different amounts of CaO

in powder and in porous pellets (13 mm diameter) for different periods of time (from 5 minutes to 4 hours). Formation of $CaSO_4$ was assessed quantitatively by XRD.

3.2. Formation of ye'elimite, $C_4A_3\bar{S}$

At ≈1200-1300 °C, $C_4A_3\bar{S}$ was formed in SO_2+O_2 atmospheres from 30 g mixes of $CaCO_3$ and Al_2O_3. Figure 2 shows the XRD pattern following 30 minutes reaction at 1220 °C, where the rates of SO_2 and air used were 0.105 and 0.2624 g/min, respectively, giving a SO_2:air ratio of 1:2.5. Such a high SO_2 concentration did not lead to high yields of ye'elimite: $CaSO_4$ forms, leaving unreacted Al_2O_3 and CaO coexisting with CA_2 and CA. The results cannot be in equilibrium as some phases are known to be incompatible, e.g. CaO and CA_2 (Galan et al. 2017). Re-introducing the sample for another 30 minutes in the furnace under the same conditions led to an increase in ye'elimite and a decrease in $CaSO_4$, leaving traces of CA_2 and Al_2O_3 still present. Further repetition of the same process led to total disappearance of CaO and Al_2O_3 and some increase both in the ye'elimite yield and reduction in the $CaSO_4$ with almost constant CA_2. After 7x30 minutes cycles, the XRD pattern did not change and it was considered that the sample reached its final state.

Rates of SO_2 and air of 0.0525 and 1.3122 g/min, respectively (ratio SO_2:air of 1:25) were used for tests of 60 minutes duration. Figure 3 shows the result of this synthesis, performed using the same amount of raw materials (stoichiometric amounts of $CaCO_3$ and Al_2O_3 to form $C_4A_3\bar{S}$) and same temperature (1220 °C) as the previous ones, for 60 minutes. As it can be seen, lower SO_2 partial pressure (10 times dilution) led to higher yields of $C_4A_3\bar{S}$, no unreacted raw materials and only small amounts of $CaSO_4$ and CA remaining. These experiments suggest the existence of a threshold in the SO_2 concentration which, if exceeded, favours reaction of SO_3 with lime to give $CaSO_4$, inhibiting formation of ye'elimite.

3.3. Formation of ternesite, $C_5S_2\bar{S}$

In a similar fashion to the methods used in section 4.2, the formation of $C_5S_2\bar{S}$ was investigated. A mix of $CaCO_3$ and SiO_2 (quartz) was prepared and placed in a boat and reacted at 1220°C for 60 minutes. As with the $C_4A_3\bar{S}$ experiments, the reactive sulfur containing atmosphere was left running for the duration of the experiment. Flow-rates of 0.25 g/min air and 0.1 g/min SO_2 were

used in the initial high SO_2 partial pressure experiment to give a ratio SO_2:air 1:2.5. Figure 4 shows that the experiment did not form ternesite and instead produced a mixture of belite, anhydrite and unreacted material. The temperature, reaction time and cooling rates of the reaction were altered in attempts to form ternesite but, at this partial pressure, these experiments proved unsuccessful.

As calculation suggested that the SO_2 partial pressure was too high, another experiment was conducted, where the partial pressure of the SO_2 component of the atmosphere was lowered, similar to what was done in section 4.2: flow-rates of 0.1 g/min SO_2 and 2.5 g/min air were used to give a ratio air:SO_2 of 25:1. As shown in Figure 5, ternesite was successfully formed at 1075 °C in the sulfur containing atmosphere for the first time, in the presence of belite, anhydrite and unreacted lime. The temperature was chosen based on previous work (Pliego-Cuervo, Glasser 1978), who synthesized ternesite in sealed systems using belite and calcium sulfate as reactants. These experiments show the combined influence of temperature and SO_2 partial pressure on the stability of sulfur-containing phases. The field of stability of ternesite has subsequently been mapped by Hanein et al. (Hanein et al. 2017) who show quantitatively the necessity of controlling the partial pressures of gas species if ternesite is the desired product.

3.4. Synthesis of clinkers using laboratory grade reactants

At 1300 °C clinkers containing ye'elimite, belite and anhydrite were synthesized from mixes of $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3 using both mixes of reactants in powder form and by pressing these same mixes in the form of 13 mm diameter pellets. The thickness of the pellets was ≈ 2 mm. Three different mixes were used in order to obtain different proportions of the phases in the final product. Targeted compositions are given in Table 2. Figure 6 and Figure 7 show the pellets corresponding to target compositions 1 and 2, respectively. In both cases the pellets were coherent and did not show cracking. However, the pellets with target composition 3, high in silica, crumbled during cooling and only powder could be retrieved.

The results from Rietveld refinement of the XRD patterns of the pellets are shown in Table 5. Mixes 1 and 2 led to formation of mainly four phases: ye'elimite, belite, anhydrite and gehlenite (C_2AS). In both cases, crystalline ferrite was almost absent. The presence of undesired $C\bar{S}$ and

C_2AS can be attributed to kinetic effects but also to the SO_2 partial pressure used which may have favoured their formation.

Mix 3 gave very different mineralogy: in this case, both β-C_2S and γ-C_2S were present, as well as ferrite and tricalcium aluminate. $CaSO_4$ was absent and $C_4A_3\bar{S}$ and C_2AS only appeared in very low percentages. The physical decomposition of pellets, termed 'dusting', is attributed to the volume expansion arising from spontaneous conversion of the high temperature belite phases to γ-C_2S in the course of cooling.

Table 6 shows the results obtained from Rietveld analysis for the clinkers synthesized using lab grade reactants including $CaSO_4$ (conditions shown in Table 3).

At a constant temperature of 1280 °C, a drastic effect is observed when diluting the SO_2 from SO_2:air ratio of 1:2.5 to 1:25 (reactions 1 and 2, respectively, in Table 6), not only in the formation of ye'elimite but also on the belite. High concentrations of SO_2 shifted the equilibrium away from belite to mixtures of $C\bar{S}$ and C_2AS. Further reduction of the SO_2 partial pressure (ratios SO_2:air 1:50 and 1:100 in reactions 3 and 4 in Table 6) did not lead to significant changes in the final compositions. The remaining % of C_2AS and C$ are attributed to kinetic effects: once C_2AS and $C\bar{S}$ formed in quantity, 120 minutes does not seem to be sufficient to completely shift compositions towards C_2S and $C_4A_3\bar{S}$.

Lower temperatures also have an impact in the final compositions, especially at the lower SO_2 partial pressure conditions (experiment 5 in Table 6) at 1230 °C and 1:50 SO_2:air ratio), making it even more difficult to reach the target compositions by reacting $C\bar{S}$ and C_2AS.

The effect of the gas flow rate is also shown in experiments 2 and 9. Similar temperature (1280 and 1270 °C, respectively) and partial pressure (SO_2:air ratio 1:25) but different gas flow rate (SO_2:air rates 0.105:2.63 and 0.088:2.204 g/min, respectively) led to different results. In this case, lower rates promoted formation of $C_4A_3\bar{S}$ and C_2S: the faster the gases passed over the solid reactants the more this reaction was suppressed.

Compositions with higher ye'elimite content, around 60%, could be achieved at temperatures as low as 1200 °C (experiment 10 in Table 6); increasing the temperature to 1250 °C led to an increase in both ye'elimite and belite contents (experiment 11 in Table 6).

The absence of ferrite in some clinkers could be attributed to the poorly crystalline ferrite, not 'visible' by XRD, the possible inclusion of some iron, probably not exceeding a few wt. %, in ye'elimite (Touzo, Scrivener & Glasser 2013), and the limitations of the XRD to detect small amounts of phases.

3.5. Synthesis of clinkers using commercial grade reactants

Table 7 and Table 8 show results of Rietveld analysis and thermodynamic modelling output, respectively, of clinkers made with commercial grade raw materials (conditions shown in Table 4).

In the experiments with raw materials dilution of the SO_2 from SO_2:air ratios of 1:25 (experiments 1 and 2 in Table 7) to 1:100 (experiments 3 and 4 in Table 7) led to a significant increase in ye'elimite and belite. Also, the yield at 1300 °C is notably higher than at 1250 °C (experiments 1-4 in Table 7).

These experiments indirectly show the effect of the presence of impurities in the raw materials which affect stability and formation of the phases giving different results and different effect of temperature and SO_2 partial pressure. The mineralogical evolution with time can be observed in experiments 5-7 in Table 7: at 1300 °C and 1:100 SO_2:air ratio, equilibrium seems to shift towards formation of ye'elimite and belite with slow disappearance of gehlenite and calcium sulfate.

According to the model predictions, the conditions used in experiments 2, 4 and 5-7 would lead to the target compositions. The reasons why these were not achieved are likely due to kinetic limitations, the ferrite not being 'visible' with XRD and possibly the cooling rate which may have favoured formation of anhydrite and gehlenite as opposed to ye'elimite and belite. It must also be noted that the model does not account for solid solutions (or liquid solutions) and can therefore not predict the formation of entropy stabilised phases such as ye'elimite with iron substitution or various aluminoferrite compositions.

The formation of ternesite is predicted in four of the compositions (2, 3, 8 and 9 in Table 8) but only detected experimentally in two (3 and 8 in Table 7). This can be understood by looking at the temperatures and partial pressures which were used. Comparing experiments 2 and 3 from

Table 4, both were carried out at SO_2:air 1:100, but at different temperature. While in the experiment at 1250 °C ternesite could be seen, 1300 °C seems to be too high for ternesite to stabilise. In experiments 8 and 9 from Table 4, both performed at 1275 °C, the lower SO_2 partial pressure, 1:100 SO_2:air ratio, favoured formation and stabilisation of ternesite as opposed to 1:50. Even though under ideal conditions ternesite would form in all cases, in reality too high temperatures and too high partial pressures make it more difficult for it to be stabilised.

4. Discussion

At present, designing and implementing an "optimum" $C\bar{S}A$ clinker is arguably more difficult than producing a PC clinker. Firstly, we do not at present know the "optimum" clinker mineralogy. Should ternesite be present, and if so how much? Can we control the polymorphism of belite so as to reproduce a reactive clinker with fast strength gain? And how are the economics of the raw materials associated with the clinker mineralogy? How do the clinker phases react with water and with each other to produce dense and durable matrices? Many questions remain unanswered.

But another complication arises: the presence of an important sulfur cycle in the course of clinkering which can affect mineralogy. These dependencies, weak for PC cements, become crucial in making $C\bar{S}A$ cement. The concept of using a reactive atmosphere to facilitate reaction kinetics and control the quantitative clinker mineralogy is crucial but has not been well explored in respect of $C\bar{S}A$ cement clinkering.

It is known that gas-solid reactions are important to a range of problems, as for example, in Portland cement clinkering, where the cycle of alkali circulation via the vapour phase may lead to condensation in cooler zones of (K, Na) sulfates on the clinker and these in turn, affect early hydration and set. However, the main oxide components of Portland cement are relatively involatile and the vapour phase composition relatively unimportant to the circulation of the main oxides. But cycles involving transfer of sulfur species assume much greater importance in the course of clinkering $C\bar{S}A$ formulations where they control mass and energy balances. Both $C_4A_3\bar{S}$ and $C_5S_2\bar{S}$ have definite limits of thermodynamic stability which need to be formulated in terms of composition, temperatures and fugacities of both SO_2 and O_2. Our approach to process development and optimisation, combining thermodynamic calculation with experimentally -

derived data, is being brought to maturity to guide and enhance clinker process development quantitatively to control clinker mineralogy.

Many commentators have expressed doubts that gas fugacities (which we equate with partial pressures) can be controlled in a rotary kiln. While this may be true as a general case, special circumstances arise in the formation of calcium sulfoaluminate clinkers which make control relatively easy to achieve. For example, conventional kilns consume the oxygen components of air with the result that the atmosphere in the burning zone has ca 1-4% free oxygen: typically an order of magnitude less than air. If the oxygen pressure is allowed to drop below that range, locally reducing conditions are generated which affect clinker quality: for example, ferric iron is reduced to ferrous. Moreover, sulfur, if present, is chemically reduced to sulfide and CO increasingly appears in exit gases. These processes are undesirable, so free oxygen is always present in excess in combustion gas. On the other hand, if oxygen partial pressures are allowed to rise, the thermal economy decreases as excess air is unnecessarily heated. Even if oxygen enriched gas is used, the same set of restrictions apply. Broadly, we assume that these considerations will also apply to C$\bar{S}$A production. Thus, we assume that the oxygen partial pressure will lie within a narrow range to optimise the clinkering process.

The sulfur species at elevated temperatures are dominated by SO_2 and its partial pressure is fixed by temperature and by the sulfur content of the raw meal and fuel. As an approximation, the vapour pressure of SO_2 in equilibrium with the clinker phases, e.g. anhydrite and ye'elimite, can be used to fix the *minimum* numerical value of the partial pressures necessary to stabilise these phases against evaporation. However, the actual pressure may significantly exceed that minimum, as for example is likely to occur in the course of combusting sulfur- rich fuels, or when elemental sulfur is injected into the kiln to supply part of the thermal energy.

Thus, we can distinguish three regimes in clinkering C$\bar{S}$A compositions: (i) a regime with low partial pressure of SO_2 in which the raw meal loses sulfur in order to saturate the kiln atmosphere, (ii) a regime which is essentially neutral and no significant loss or gain of sulfur occurs between solid and atmosphere and finally (iii), a regime mainly of higher SO_2 pressures in which sulfur, effectively as "SO_3", is transferred from the atmosphere to the solid. In order for regime (iii) to operate, excess oxygen has to be present because, as noted, the transfer of sulfur

from vapour to solid also involves an oxidation of the sulfur from S(IV) to S(VI). However, this condition is readily achieved by an excess of oxygen in the kiln atmosphere.

Despite the limitations of the experimental set-up, it was successfully proven that the transfer of SO_2 and O_2 gas to the clinkering solids to form $C\bar{S}A$ clinkers occurs rapidly and efficiently under normal operating conditions. It is also shown that clinkering temperatures tend to fall within a narrow range. At temperatures below ≈1230 °C, reaction kinetics are too slow to achieve complete reaction in the normal residence time in the hot zone, ca 20-60 minutes. On the other hand, if it is desired to produce ternesite, which decomposes above an estimated 1298 °C (Gutt, Smith 1967), clinkering temperatures cannot exceed this limit and the sulfur pressures need to be maintained within limits determined by Hanein, et al (Hanein et al. 2017). If the limits are observed, ternesite rich clinkers can be made in a single stage operation. However, ternesite can only be considered as a desirable clinker mineral if, in clinker, its reactions with other minerals and water leads to rapid strength gain: at present, this is not fully assured.

Ye'elimite containing clinkers have similar restrictive ranges where kinetics and equilibrium allow it to form stably, but these limits are in general somewhat less restrictive than those of ternesite. Above ≈ 1320 °C extensive melting occurs, so, depending on the target mineralogy, clinkering temperatures will also lie in a narrow band between about 1250 and 1320 °C. The other key variable, the partial pressure of SO_2, greatly affects the mineralogy of the clinkers: at a given temperature (around 1250-1300) a threshold in SO_2 partial pressure exists above which $C\bar{S}$ and C_2AS are more favourable to form than $C_4A_3\bar{S}$ and C_2S.

What is under less good control are the rates of sulfur transfer and their relation to the state or condition of the gas- solid surface available for exchange. These are functions of, amongst other factors, kiln size, gas flow rates and countercurrent solid flow rates, as well as total mass of transferrable components. As such these factors are probably specific to specific equipment and are not readily calculated without process data.

In this way, by combining technical and thermodynamic limits, it is possible to control the kiln atmosphere simply by controlling the sulfur content of the fuel and raw mix and ensuring an excess of oxygen.

The knowledge gained from these experiments and calculations, that is, the influence of temperature and partial pressures of the gaseous components informed the pilot plants trials at Ibutec, Weimar, Germany, reported in (Hanein et al. 2016).

Another important aspect of this work, controlling the polymorphism and reactivity of belite, is still work in progress (Elhoweris, Galan & Glasser 2017). And, of course, hydration studies are needed to determine the properties of the resulting binders at all ages. The correlation of clinker mineralogy with cementing properties is under investigation (Jen et al. 2017).

5. Conclusions

Experiments show that SO_2 and oxygen in the vapour are readily transferred to calcium aluminates and silicates thereby combining much of the sulfur. Understanding the physical chemistry of the process enables control over clinker phase composition and avoids production of free lime, arising from decomposition of anhydrite and aluminates. The method emphasises mass gains as opposed to more usual mass losses, which give greater freedom to design $C\bar{S}A$ clinkers with optimised properties and utilise sulfur containing fuel whose heat of combustion enables decrease consumption of hydrocarbon fuel and lowered CO_2 emissions.

Thermodynamic modelling has proven to be an invaluable tool with which to simulate, evaluate and optimise novel cement compositions.

Acknowledgements

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Figure captions

Figure 1. Furnace used for the experiments where sulfur was transferred from the gas to the solid phase. The entire unit is housed in a ventilated enclosure 2400 mm width x 640 mm depth. Note the red bar which is an edge of the sliding glass screen shown here in its open position.

Figure 2. Synthesis of ye'elimite from $CaCO_3$ and Al_2O_3 in an atmosphere of SO_2+air (ratio SO_2:air of 1:2.5) at 1220 °C. Result after 30 minutes reaction.

Figure 3. Synthesis of ye'elimite from $CaCO_3$ and Al_2O_3 in an atmosphere of SO_2+air (ratio SO_2:air of 1:25) at 1220 °C for 60 minutes.

Figure 4. Attempt to synthesize calcium sulfosilicate in an atmosphere of SO_2+air (ratio SO_2:air of 1:2.5) at 1220 °C for 60 minutes.

Figure 5. Formation of calcium sulfosilicate from C_2S and $C\bar{S}$ in an atmosphere of SO_2+air (ratio SO_2:air of 1:25) at 1075 °C for 60 minutes.

Figure 6. Pellets with target composition 1 (Table 2) after firing at 1300 °C for 30 minutes under SO_2+air atmosphere (ratio SO_2:air of 1:2.5). Pellets are 13 mm diameter.

Figure 7. Pellets with target composition 2 (Table 2) after firing at 1300 °C for 30 minutes under SO_2+air atmosphere (ratio SO_2:air of 1:2.5). Pellets are 13 mm diameter.

Table captions

Table 1. Oxide composition of raw materials used for the experiments. XRF measurements of bauxite and clay were performed at Edinburgh University at the School of Geosciences. Oxide composition of limestone was provided by the supplier (Samin).

Table 2. Experimental conditions used for clinkers made with mixes of $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3.

Table 3. Experimental conditions used for clinkers made with mixes of $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and $CaSO_4$.

Table 4. Experimental conditions used for clinkers made with commercial grade raw materials.

Table 5. Rietveld analysis results of clinkers synthesized from laboratory grades of $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3: experimental conditions shown in Table 2. Note the polymorphs of $C_4A_3\bar{S}$ and C_2S are included in the corresponding boxes. O and C stand for orthorhombic and cubic ye'elimite, and α', β and γ are the three polymorphs of C_2S. wRp stands for weighted-profile R factor.

Table 6. Rietveld analysis results of clinkers synthesized from laboratory grades of $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and $CaSO_4$: experimental conditions shown in Table 3. Note the polymorphs of $C_4A_3\bar{S}$, orthorhombic (O) and cubic (C), are included in the corresponding box. All C_2S formed in these experiments was β-C_2S.

Table 7. Rietveld analysis results of clinkers synthesized from commercial grade raw materials clay, bauxite and limestone: experimental conditions shown in Table 4. Note the polymorphs of $C_4A_3\bar{S}$ and C_2S are included in the corresponding boxes. O and C stand for orthorhombic and cubic ye'elimite, and α' and β for the polymorphs of C_2S.

Table 8. Model predictions for the clinker compositions made with commercial grade raw materials: clay, bauxite and limestone. Temperature and gas atmosphere used for the simulations are detailed in Table 4.

Figure

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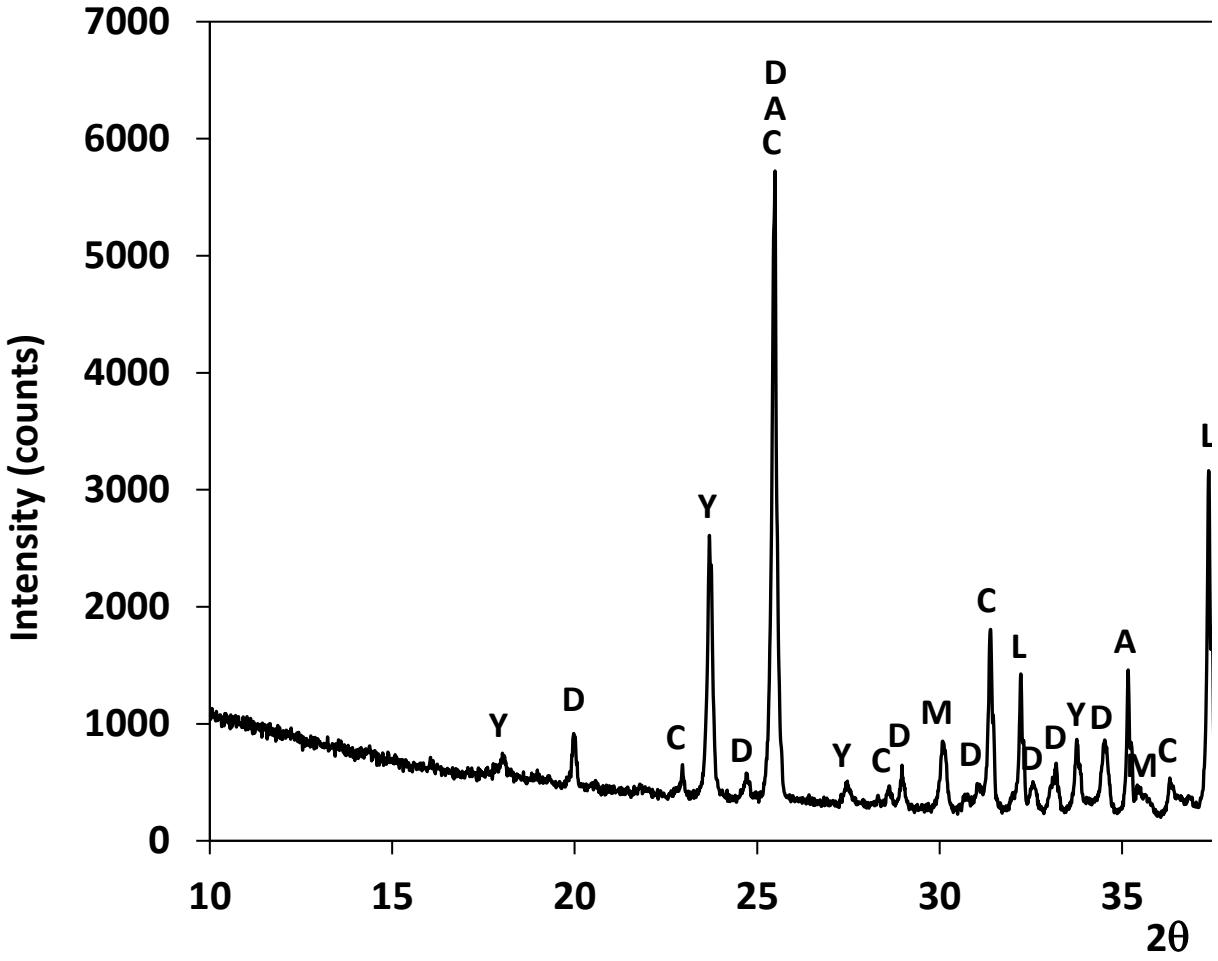
Figure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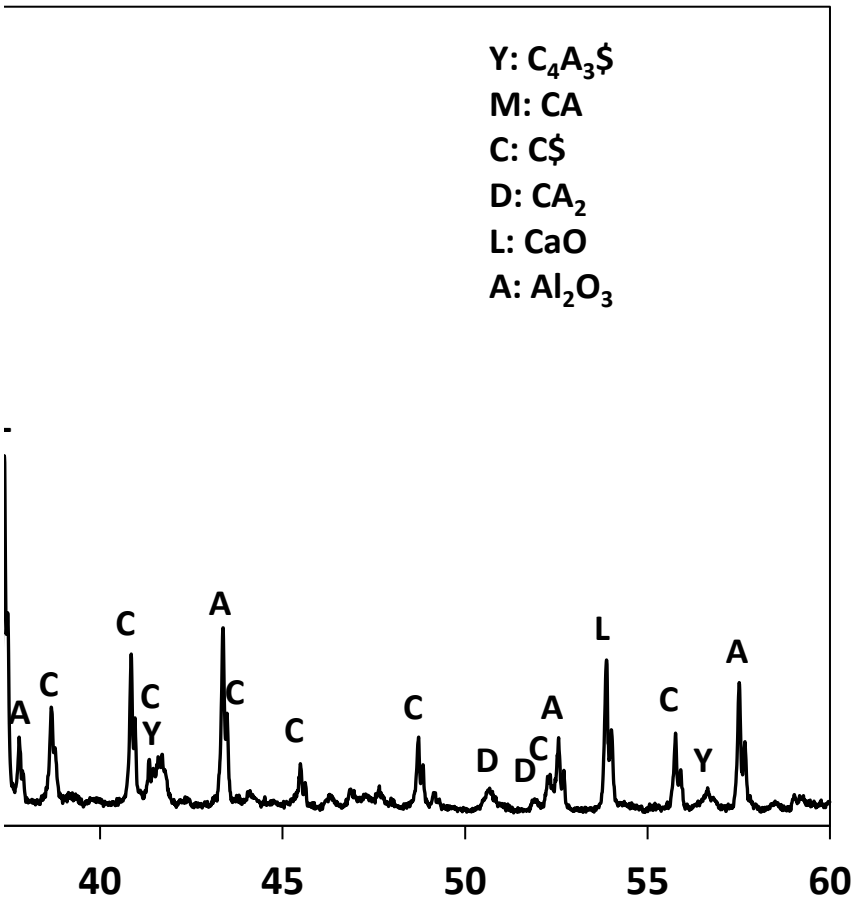
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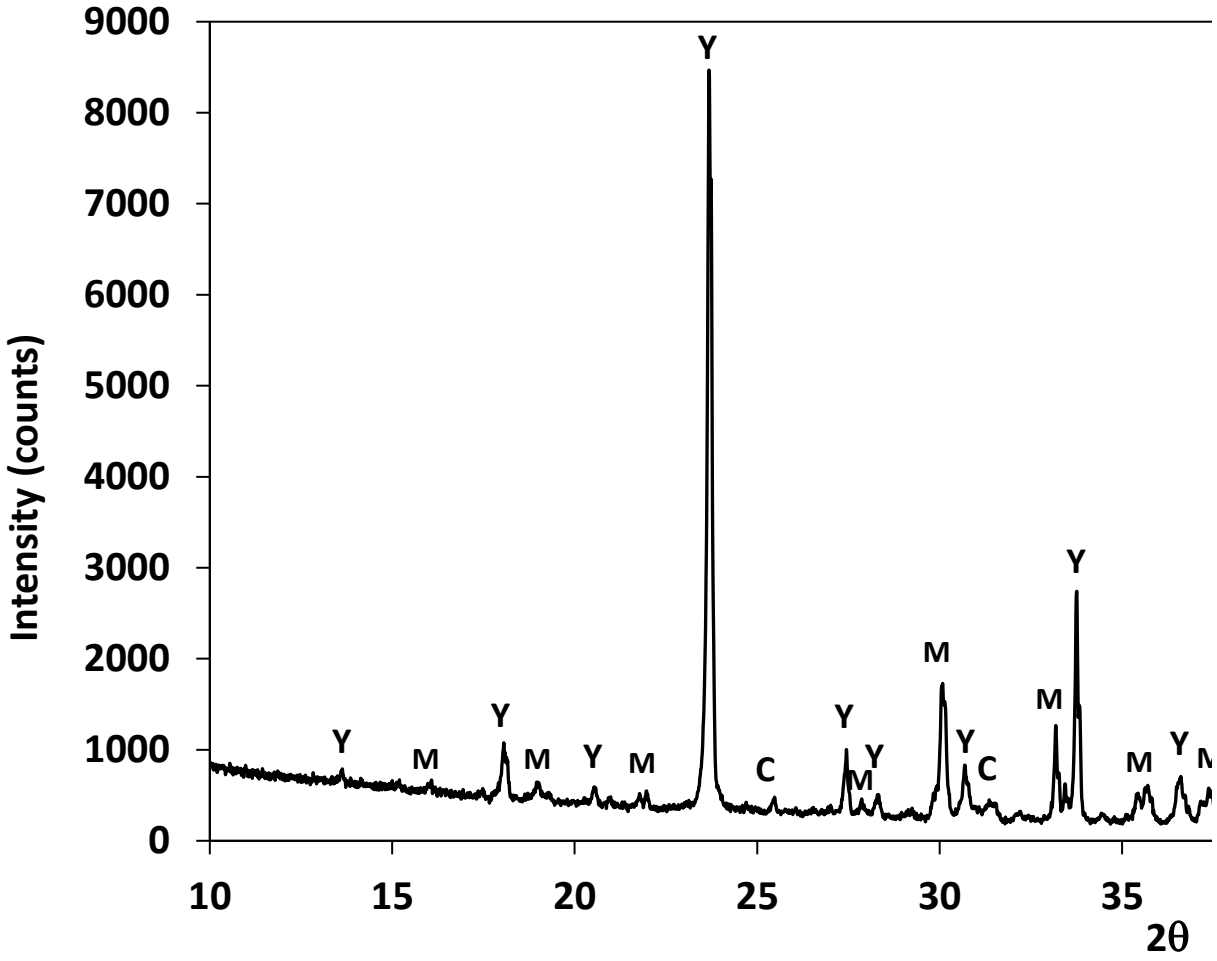
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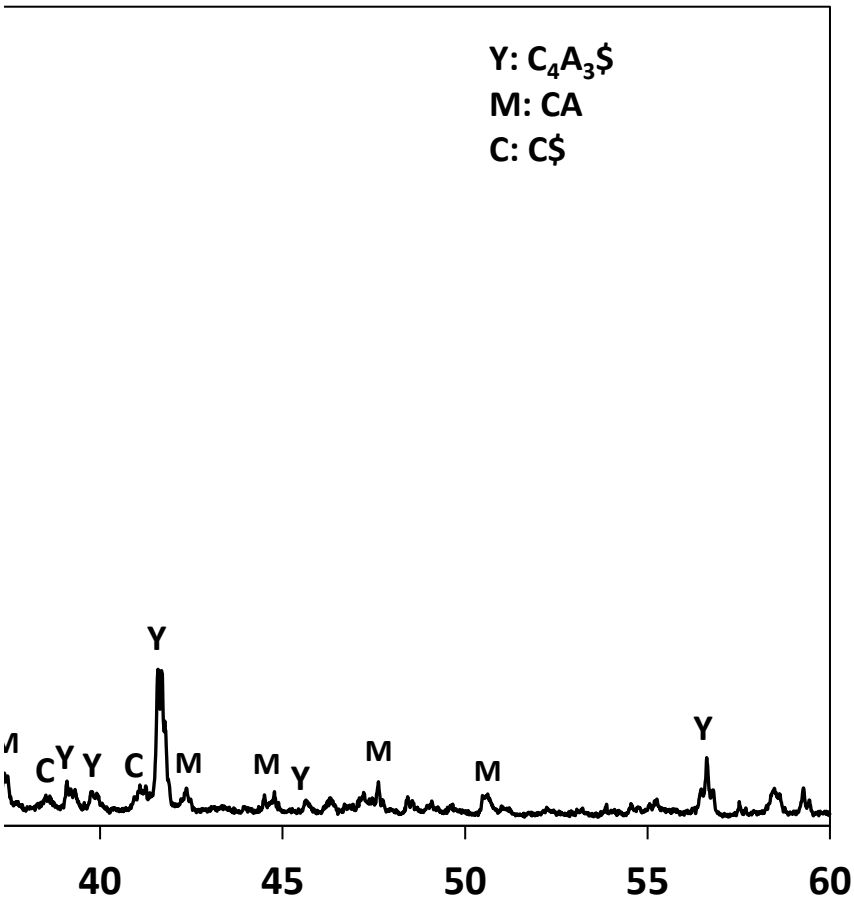
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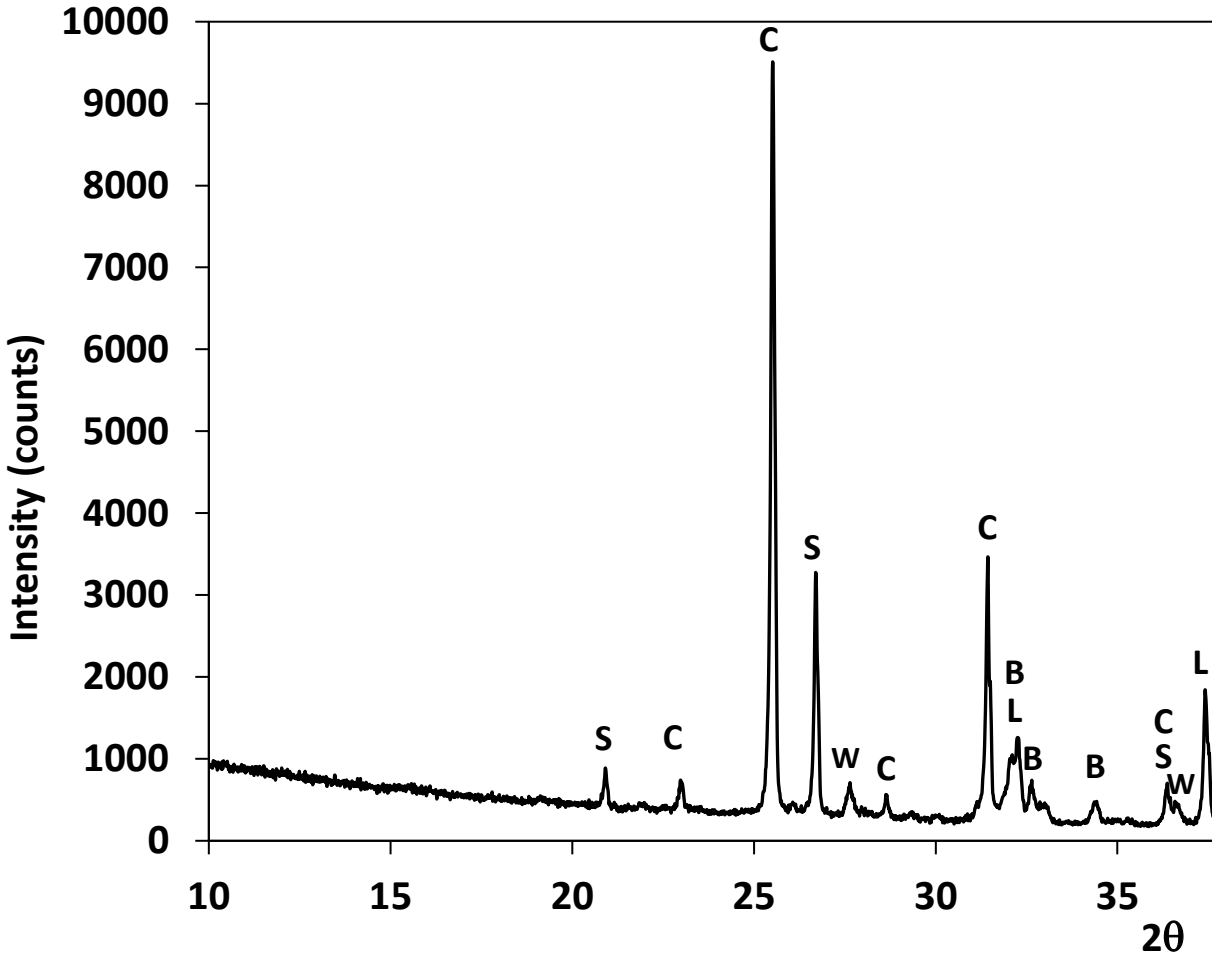
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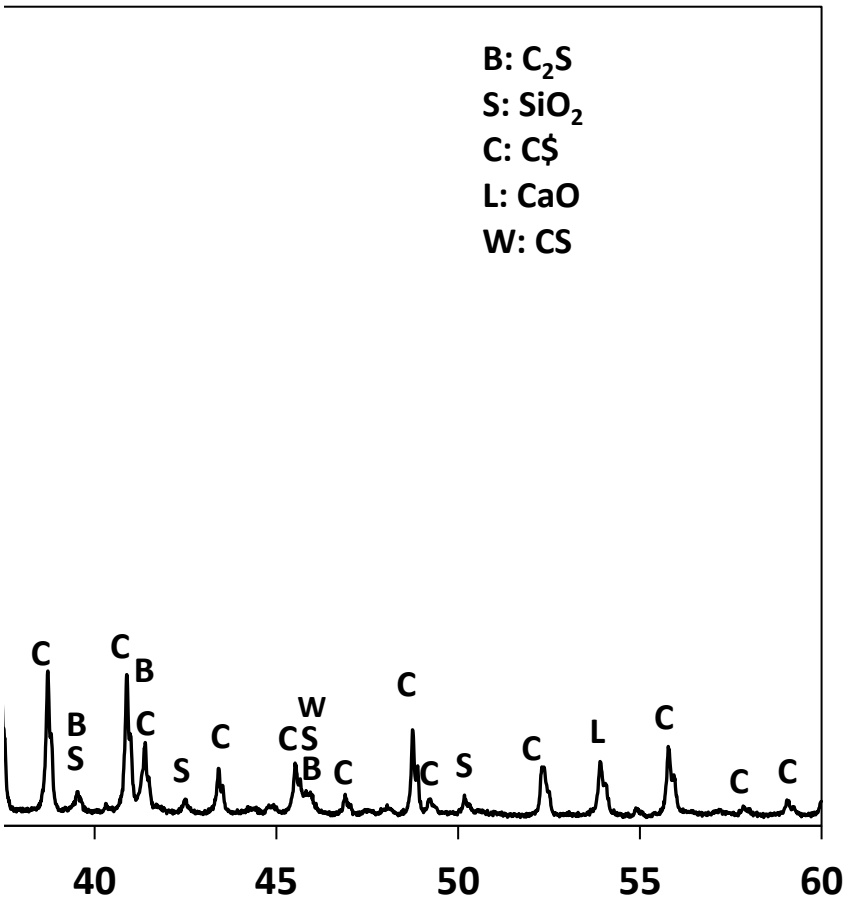
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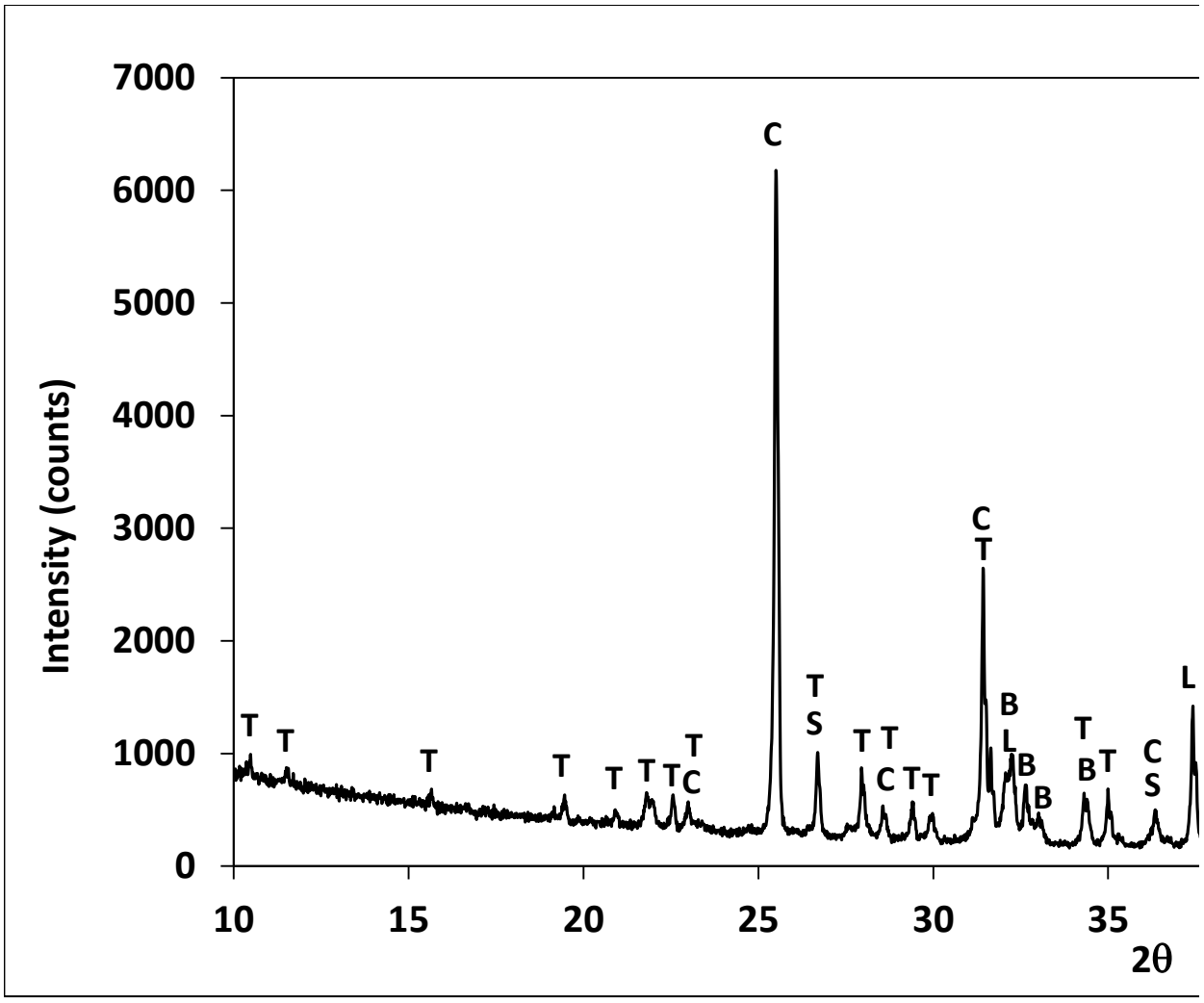
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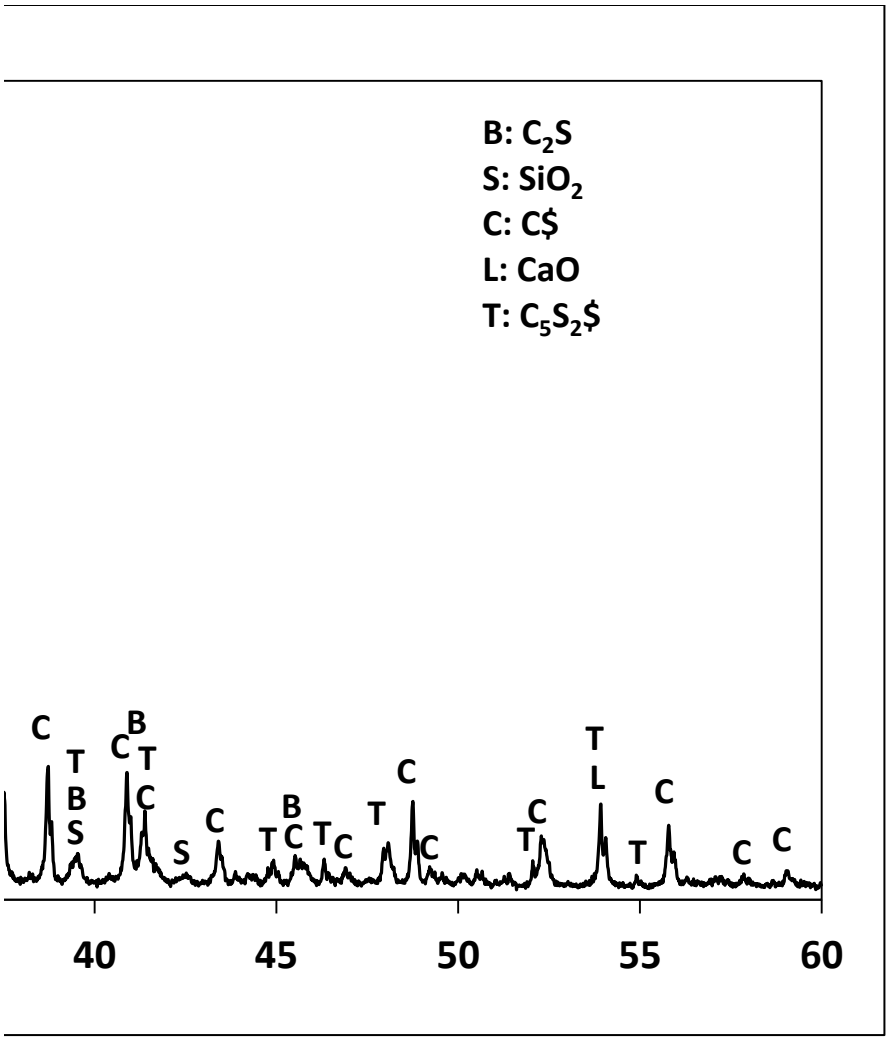
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Figure

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Figure

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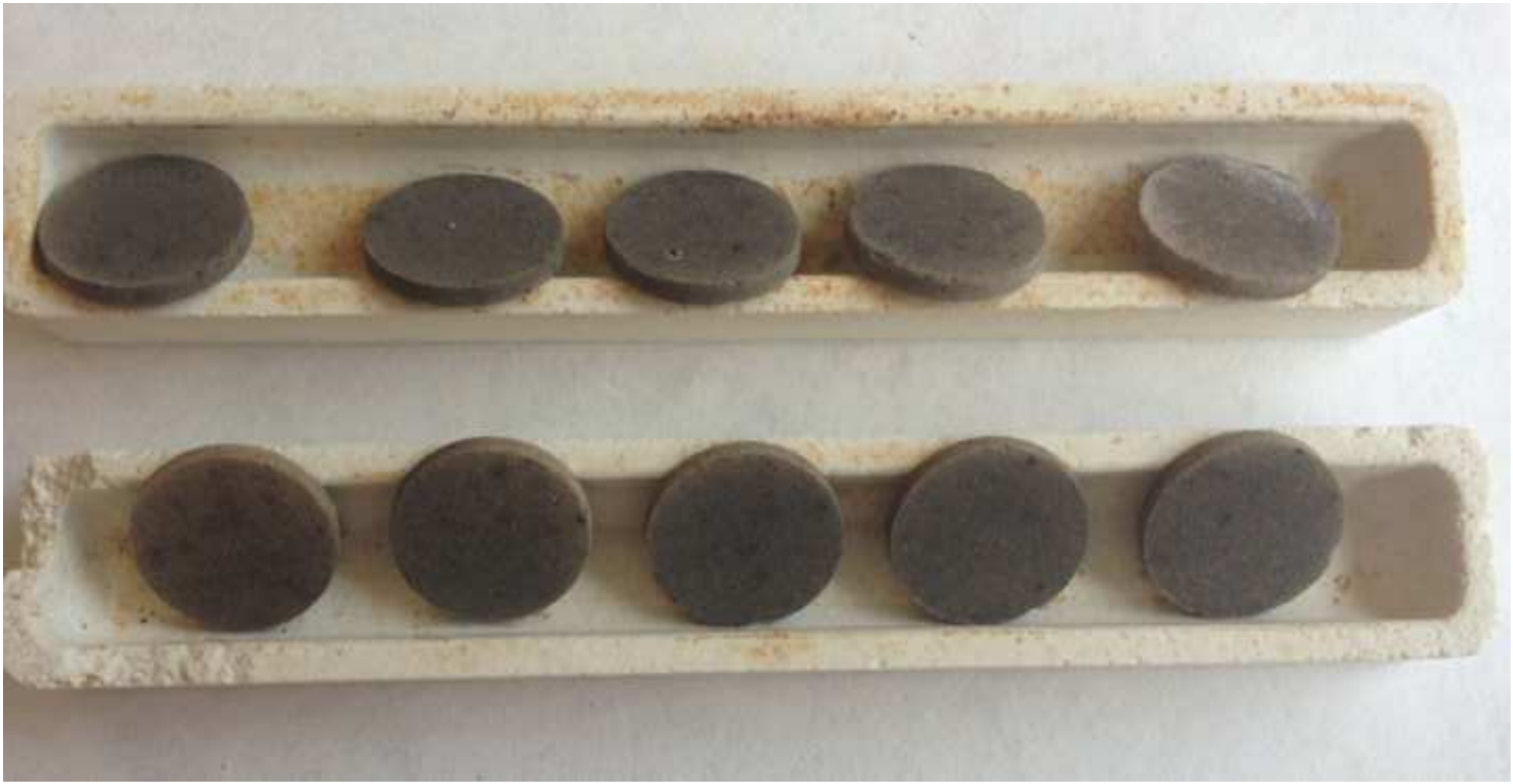

Table 1. Oxide composition of raw materials used for the experiments. XRF measurements of bauxite and clay were performed at Edinburgh University at the School of Geosciences. Oxide composition of limestone was provided by the supplier (Samin).

% Oxides	Bauxite	Clay	Limestone
SiO_2	11.52	39.24	0.1
Al_2O_3	69.32	38.18	0.00
Fe_2O_3	1.21	5.98	0.009
MgO	0.00	0.06	0.26
CaO	0.16	0.87	55.70
Na_2O	0.00	0.00	0.00
K_2O	0.455	0.624	0.00
TiO_2	3.409	1.773	0.00
MnO	0.000	0.001	0.00
P_2O_5	0.081	0.088	0.00
LOI	13.44	13.08	44.00

Table 2. Experimental conditions used for clinkers made with mixes of $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3.

	Target mineralogy (weight %)	Input (weight % solids)	Mass flow rates SO_2:air (g/min)	Temperature (°C)
1	60% $C_4A_3\$$ 20% C_2S 20% C_6A_2F	48.1% CaO 7.6% SiO_2 37.2% Al_2O_3 7.1% Fe_2O_3	0.04:0.1 (1:2.5)	1300
2	40% $C_4A_3\$$ 40% C_2S 20% C_6A_2F	52.7% CaO 14.7% SiO_2 25.6% Al_2O_3 6.9% Fe_2O_3	0.04:0.1 (1:2.5)	1300
3	20% $C_4A_3\$$ 60% C_2S 20% C_6A_2F	57.1% CaO 21.5% SiO_2 14.6% Al_2O_3 6.8% Fe_2O_3	0.04:0.1 (1:2.5)	1300

Table 3. Experimental conditions used for clinkers made with mixes of $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and $CaSO_4$.

	Target mineralogy (weight %)	Input (weight %)	Mass flow rates SO_2:air (g/min)	T (°C)
1	30% $C_4A_3\$$ 60% C_2S 10% C_6A_2F	52.1% CaO 20.9% SiO_2 6.7% $CaSO_4$ 18.0% Al_2O_3 2.3% Fe_2O_3	1.05:2.63 (1:2.5)	1280
2			0.105:2.63 (1:25)	
3			0.1:5 (1:50)	
4			0.04:4 (1:100)	
5			0.04:2 (1:50)	1230
6			0.04:1 (1:25)	1230
7			0.088:2.204 (1:25)	1200
8				1250
9				1270
10	60% $C_4A_3\$$ 30% C_2S 10% C_6A_2F	40.9% CaO 10.5% SiO_2 13.4% $CaSO_4$ 33.0% Al_2O_3 2.3% Fe_2O_3	0.088:2.204 (1:25)	1200
11				1250

Table

Table 4. Experimental conditions used for clinkers made with commercial grade raw materials.

	Target mineralogy (weight %)	Input (weight %)	Flow rates SO_2:air (g/min)	Temperature (°C)	Time (min)
1	36% $C_4A_3\$$ 32% C_2S 9% C_4AF 23% C$	12.2% bauxite 68.4% limestone 19.5% clay	0.04:1 (1:25)	1250	120
2				1300	
3			0.04:4 (1:100)	1250	
4				1300	
5	34% $C_4A_3\$$ 42% C_2S 11% C_4AF 13% C$	6.6% bauxite 67.3% limestone 26.1% clay	0.04:4 (1:100)	1300	120
6					60
7					30
8				1275	120
9			0.04:2 (1:50)		

Table 5. Rietveld analysis results of clinkers synthesized from laboratory grades of $CaCO_3$, SiO_2, Al_2O_3 and Fe_2O_3: experimental conditions shown in Table 2. Note the polymorphs of $C_4A_3\$$ and C_2S are included in the corresponding boxes. O and C stand for orthorhombic and cubic ye'elimite, and α', β and γ are the three polymorphs of C_2S. wRp stands for weighted- profile R factor.

	Target mineralogy (weight %)	Output mineralogy (weight %)								wRp (%)
		$C_4A_3\$$	C_2S	$C\$$	C_2AS	C_4AF	S	C_3A	$C_{12}A_7$	
1	60% $C_4A_3\$$ 20% C_2S 20% C_6A_2F	O 20 C 28	α' 1 β 2	23	26	1				5.28
2	40% $C_4A_3\$$ 40% C_2S 20% C_6A_2F	O 15 C 23	α' 2 β 19	18	21	1				4.99
3	20% $C_4A_3\$$ 60% C_2S 20% C_6A_2F	O 2	β 25 γ 18		1	28	4	20	1	5.48

Table 6. Rietveld analysis results of clinkers synthesized from laboratory grades of $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3 and $CaSO_4$: experimental conditions shown in Table 3. Note the polymorphs of $C_4A_3\$$, orthorhombic (O) and cubic (C), are included in the corresponding box. All C_2S formed in these experiments was β-C_2S.

	Target mineralogy (weight %)	Output mineralogy (weight %)									wRp (%)
		$C_4A_3\$$	β-C_2S	$C\$$	C_2AS	$C_5S_2\$$	CA	C_4AF	C	S	
1	30% $C_4A_3\$$ 60% C_2S 10% C_6A_2F	O 1 C 4		57	38						5.68
2		O 17 C 12	33	16	22						5.57
3		O 19 C 13	37	12	19						4.72
4		O 15 C 19	33	11	21						5.74
5		O 9 C 10	13	41	13	4	7	1		2	8.33+
6		O 24 C 11	35	12	5	2		4	4	2	5.23
7		O 23 C 8	21	24	4	8		3	6	4	6.00
8		O 15 C 14	32	21	14	4					5.89
9		O 27 C16	40	13	5						5.70
10	60% $C_4A_3\$$ 30% C_2S 10% C_6A_2F	O 43 C 15	8	17	2	4	4	2	4		5.81
11		O 63	14	16	7						9.22

Table 7. Rietveld analysis results of clinkers synthesized from commercial grade raw materials clay, bauxite and limestone: experimental conditions shown in Table 4. Note the polymorphs of $C_4A_3\$$ and C_2S are included in the corresponding boxes. O and C stand for orthorhombic and cubic ye'elimite, and α' and β for the polymorphs of C_2S.

	Target mineralogy (weight %)	Output mineralogy (weight %)						wRp (%)
		$C_4A_3\$$	C_2S	$C\$$	C_2AS	CT	$C_5S_2\$$	
1		O 1 C 4		64	31	1		9.46
2	36% $C_4A_3\$$ 32% C_2S	O 8 C 13	β 4 α' 2	48	25		1	9.30
3	9% C_4AF 23% $C\$$	O 20 C 17	β 11 α' 7	29	4	2	11	6.79
4		O 30 C 16	β 23 α' 8	22		1	0	5.63
5		O 22 C 20	β 28 α' 3	23		5		8.46
6		O 10 C 32	β 23 α' 3	27	3	3		8.63
7	34% $C_4A_3\$$ 42% C_2S 11% C_4AF 12% $C\$$	O 13 C 23	β 19 α' 2	32	9	1	2	6.93
8		O 8 C 25	β 9	27	11	1	18	6.60
9		O 1 C 1		59	39			10.62

Table 8. Model predictions for the clinker compositions made with commercial grade raw materials: clay, bauxite and limestone. Temperature and gas atmosphere used for the simulations are detailed in Table 4.

	Model Output (weight %) using raw materials							
	$C_4A_3\$$	C_2S	$C\$$	C_4AF	$C_5S_2\$$	CT	CF (L)	MgO
1	38.7	-	12.8	-	44.5	1.6	2.2	0.2
2	37.2	32.4	23.5	5.0	-	1.6	-	0.2
3	37.2	-	10.7	5.0	45.2	1.6	-	0.2
4	37.2	32.4	23.5	5.0	-	1.6	-	0.2
5	35.6	42.0	14.0	6.6		1.5	-	0.3
6	35.6	42.0	14.0	6.6		1.5	-	0.3
7	35.6	42.0	14.0	6.6		1.5	-	0.3
8	35.6	6.4	-	6.6	49.6	1.5	-	0.3
9	35.6	6.4	-	6.6	49.6	1.5	-	0.3

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To the editor and referees,

Enclosed is a manuscript to be considered for publication in ”Advances in Cement Research”, entitled ‘Advances in clinkering technology of calcium sulfoaluminate cement’.

The manuscript describes a new process to produce cement. The main highlight of the process is the use of sulfur, in gas phase, as a raw material to produce calcium sulfoaluminate clinkers. The method presents important advantages in terms of CO2 and energy savings. The experimental design to develop the new method is described. The experimental and thermodynamic modelling results presented here lead to the completion of pilot plant trials (published in ACR vol 28, 2016).

We appreciate your consideration and look forward to its publication.

Yours sincerely,

Isabel Galan, Ammar Elhoweris, Theodore Hanein, Marcus Bannerman, Fredrik P. Glasser