Lowering the carbon footprint and energy consumption of cement production: A novel Calcium SulfoAluminate cement production process

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Abstract

The development of novel clinker compositions or alterations to kiln process conditions is usually a slow and incremental process. The uncertainty in the effects of any change has led to the cautious development and optimization of clinker production. This work demonstrates that the pace of change can be greatly accelerated by combining the theoretical predictions of computational thermodynamics with focused experimental research. The production of Calcium SulfoAluminate (C$A) cement via a novel process substituting traditional carbon-based fuels by elemental sulfur and/or sulfur-rich fuels is used as an example.

The combustion of sulfur in the kiln is attractive as it sequesters unwanted sulfur byproducts inside a valuable and stable product (the clinker). The thermal energy of the sulfur combustion also lowers the fuel requirements and thus the CO_2 emitted by the process. The chemical feasibility, benefits, and process economics of direct combustion of these "alternative" sulfur fuels for both energy and as the sulfur trioxide source in C$A cement clinker are presented. Due to the reduced calcium content of C$A, CO_2 emissions of calcination are reduced by up to 35% using this technology. Sulfur-rich hydrocarbon fuels contain a variety of forms of sulfur. Using elemental sulfur as a surrogate demonstrates significant reductions in theoretical heat of clinkerization. If the sulfur is in a form equivalent to H_2S and the kiln process is integrated with a wet-limestone scrubber, the theoretical heat of the C$A clinkering process can even become negative implying that the energy of the carbon content of the fuels would only be required to partially offset heat losses within the production process. Pilot plant trials using elemental sulfur are shown to conform to predictions and illuminate some of the kinetic aspects which cannot be captured by equilibrium models. This demonstrates that producing C$A cement via sulfur combustion is an attractive and feasible technology with significant environmental benefits.

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I. INTRODUCTION

Climate change is an issue of global prominence and its mitigation is at the heart of the Cement Sustainability Initiative (CSI): a global effort by 25 major cement producers operating under the umbrella of the World Business Council for Sustainable Development (WBCSD). The CSI has instigated several projects to tackle the problems of climate change and sustainability such as: "Getting the Numbers Right" (GNR) [1], which aims to achieve accurate monitoring of CO_2 emissions and energy performance, and the "Carbon emissions reductions up to 2050" [2] roadmap. More recently, the WBCSD launched the "Low Carbon Technology Partnership initiative" (LCTPi) [3] for cement which extends beyond CSI members and aims to reduce CO_2 emissions in the range of 20–25% by 2030.

The world demand for cement was 2.6Gt in 2006 [2], is estimated to be ≈3.5Gt in 2015 [4], and is projected to be ≈4.4Gt in 2050 [2]. In 2006, the CO_2 emissions were 0.84t CO_2 per ton of clinker (0.66t CO_2 per ton of cement) [1]. However, the GNR values at the time only covered 31% of the world cement production mainly due to lack of coverage in China where only ≈5% of cement production was considered in the GNR database [1]. Today, the cement industry accounts for 5–8% of global CO_2 emissions, which are contributed to by the decomposition of limestone (60%) and combustion of fossil fuels (40%) [3]. The LCTPi has outlined seven action plans [3] to achieve the reduced emissions target: (1) enhance the sector's CO_2 emissions and energy consumption database, (2) enhance overall energy efficiency, (3) scale up the use of alternative fuels, (4) reduce the clinker content of cements, (5) develop novel, low-carbon cements, (6) engage the sector to identify emissions from the use of cement and concrete products that have been avoided, and (7) evaluate the opportunities of cross-sectoral initiatives such as carbon capture storage and usage (CCS-U). This study concerns two of these action plans, (3) and (5), which are combined and demonstrates that the reduced emissions targets can be achieved more rapidly than expected by using computational tools, combining calculation with focused experimental research.

II. C$A CEMENT AS AN ALTERNATIVE LOW CARBON FOOTPRINT CEMENT

Ordinary Portland Cement (OPC) is the most common type of hydraulic cement in general use around the world. Numerous alternative cementitious binders to OPC have been proposed to reduce the associated emissions of CO_2, including alkali activated cement [5], magnesia cement [6], Calcium Aluminate cement [5], Calcium SulfoAluminate (C$A) cement [5], Calcium SulfoAluminate-Ternesite cement [7] and/or various blends of these cements. The major challenges of introducing alternative cements to market are developing the production technique, ensuring the chemical and physical performance, and establishing standards. Of all the alternatives to OPC, C$A cement is the most promising and has been found to perform equally well or even exceed performance of OPC in many applications [6, 8-10]. C$A cement has been produced at commercial scale in China since the 1970s, but the reliance on bauxite as the source of alumina has constrained growth. China has also developed standards for C$A cement that could be usefully adapted for other regions of the world, e.g., see Ref. [11].

Compositionally, the difference between C$A and OPC cement is that the former is based on a different mineralogy, containing ye'elimite ($C_4A_3\$$) rather than alite (C_3S) as the major constituent [5]; belite (C_2S) and ferrite ($C_2(A,F)$) are common to both cements. N.B. All cement clinker phases are written in cement notation, see Table 1.

From the perspective of climate change, the major significance of C$A cement is the lower CO_2 emissions per unit clinker relative to OPC; both in its "raw material" CO_2 emissions (RM-CO_2) and the "fuel derived" CO_2 emissions (FD-CO_2) [12]. Given that the majority of the calcium in cements comes from the calcination of limestone (primarily $CaCO_3$), a significant reduction of RM-CO_2 emissions of C$A cement compared to OPC arises from the lower weight content of calcium in the major phases (see Table 2). In fact, using $CaSO_4$ (as opposed to $CaCO_3$) as a raw material provides an even lower carbon footprint as the sulfur will be sequestered in the final product; however, generation of $CaSO_4$ (when created as a byproduct of the energy industry) typically requires the de-carbonation of limestone thus it may have some inherent CO_2 emission associated with its production.

C$A cement also displays a significant reduction of fuel derived (FD-CO_2) emissions due to the reduced thermal energy consumption when compared to OPC. This primarily arises due to the lower clinkering temperature which is approximately 200°C less than that of OPC [13, 14]; however additional reductions in FD-CO_2 due to changes in theoretical heat and other factors are discussed in detail in the later sections.

There are several indirect CO_2 savings of C$A cement which are not directly associated with the change in clinker chemistry. For example, C$A clinker is easier to grind than OPC clinker [9] leading to a reduction in indirect CO_2 emissions through lower electrical energy requirements. C$A cement is also less dense than OPC cements by around ≈7% (as measured for a commercial C$A cement [15]) which suggests a further reduction in indirect CO_2 emissions through transportation of cement on a constant volume basis.

Table 1. Cement notation used in this work.

Oxide	CaO	SiO$_2$	SO$_3$	Fe$_2$O$_3$	Al$_2$O$_3$	CO$_2$
Notation	C	S	$	F	A	C'

Table 2. Specific raw material CO_2 emissions of various cement clinker phases. Extended from Ref. [12].

Phase	Raw materials	g CO$_2$/ g phase
C$_4$A$_3$\$	CC' + A + C\$	0.216
C$_4$A$_3$\$	CC' + A + \$ from combustion	0.288
C$_4$AF	CC' + A + F	0.362
C$_5$S$_2$\$	CC' + S + C\$	0.366
C$_5$S$_2$\$	CC' + S + \$ from combustion	0.457
C$_3$A	CC' + A	0.489
C$_2$S	CC' + S	0.511
C$_3$S	CC' + S	0.578

Cement manufacturers are often concerned by the cost of the higher alumina content of C\$A clinker [Table 3]. Demand for bauxite for aluminum production ensures it retains a higher price than the more common siliceous clays and shales used in cement production; however, it is envisioned that future formulations of C\$A clinker will be optimized to fully benefit from the alumina content of selected but abundant clays and other industrial byproducts. It has recently been shown that it is possible to replace aluminum oxide and/or hydroxide in the raw meal completely by industrial byproducts [16].

In summary, C\$A cements offer many direct and indirect reductions in CO_2 which may achieve the environmental goals outlined in the introduction. In the following section, the potential advantages of using sulfur as a fuel source for C\$A production are calculated.

III. ELEMENTAL SULFUR AND "SOUR" OIL AND GAS AS ALTERNATIVE FUELS IN CEMENT PRODUCTION

Almost all of the elemental sulfur produced today arises as a result of the Claus process employed during the desulfurization of sour oil and gas. The world production of sulfur is 72.4 Mt [18] and is rising due to an increasing reliance on sulfur-containing resources and environmental restrictions, most notably the low sulfur levels required in refined products such as diesel. Strigac and Majling [19] have demonstrated that sulfur dioxide (a combustion product of sulfur) and oxygen are readily transferred from the gas phase to C-S-A-F solid oxides to form ye'elimite and we have recently confirmed this in pilot-scale trials [20]. Sulfur also has the thermal content to fully replace the fuel used in the production of clinker as it has a heat of combustion per unit volume of combustion products comparable to that of natural gas. As an alternative zero-carbon (at the point of use) fuel, the combustion of sulfur lowers the CO_2 partial pressure in the kiln thus increasing the thermodynamic driving force for the decomposition of limestone while also

lowering the driving force for the formation of spurrite (C_5S_2C'), which is an undesirable intermediate product in clinker pyro-processing. Spurrite has been held responsible for clinker ring formation in kilns [21] which impede the optimal operation of the kiln. Sulfur and sulfur-containing fuels can also achieve the flame temperatures required for clinkering. For example, at STP with stoichiometric dry air, the flame temperature of elemental sulfur is 1973 K and for H_2S gas (which is common in organic sulfur fuels) it is 2118 K. The combustion of elemental sulfur and H_2S within sour hydrocarbon fuels produces SO_2 which may be oxidized to hexavalent sulfur and incorporated into the produced clinker, thus lessening environmental concerns over its release. It is not possible to exactly estimate the economics of using elemental sulfur as a fuel due to the large fluctuations in price [22] [Fig. 1.]; however, in 2004 each percent by weight of sulfur in crude oil lowered the oil price by 5.6% [23]. Finally, C\$A has a lower enthalpy of reaction when compared to OPC clinker thus combusting sulfur and/or sour fuels for its production provides the opportunity for significantly reduced CO_2 emissions and production costs. The arguments presented provide a convincing case for a novel process technology for the production of C\$A cement [24] where sulfur and/or "sour" fuels are used as alternatives to conventional carbon-based fuels.

Table 3. The alumina content of individual clinker phases and overall values for C\$A and OPC clinkers.

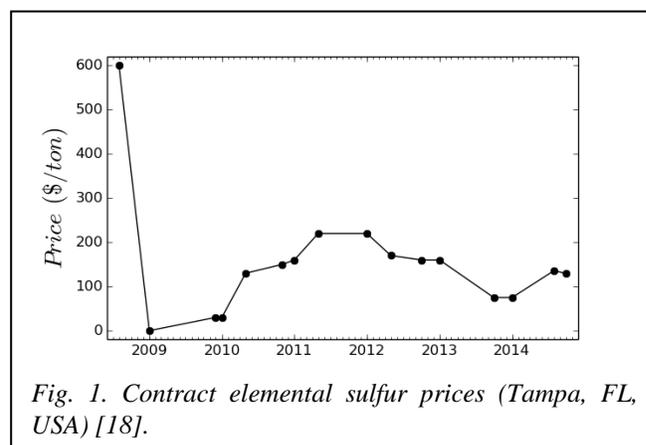| Phase	C$_4$A$_3$\$	C$_4$AF	C$_3$A	OPC [17]	C\$A
g Al$_2$O$_3$/ g	0.50	0.21	0.38	0.03-0.07	0.17-0.37

Fig. 1. Contract elemental sulfur prices (Tampa, FL, USA) [18].

IV. THEORETICAL HEAT REQUIREMENTS AND THE ECONOMICS OF PRODUCING C$A CEMENT

The theoretical heat requirements of cement clinkering are now calculated by comparing the enthalpies of the raw materials and the produced products (including gases) at STP. This method under-estimates the true energy required for production as inefficiencies prevent full heat recovery, particularly in the gas stream; however, this method is a fair basis for comparison of OPC and C$A, particularly as C$A has a lower clinkering temperature. As a basis for comparison, it is assumed that the representative theoretical heat of OPC clinker is 1760 kJ/kg and its CaO content is 67% [12, 17]. The theoretical heat required for the production of C$A clinker will be derived from thermodynamics in the following way: C$A clinker is assumed here to comprise of three stoichiometric phases, 10% C_4AF with ye'elimite and β-belite in varying proportions. A range of ye'elimite compositions are explored in this study within the range of 30-70% which is typical for C$A [5]. The reference heat of formation at STP of ye'elimite is calculated using the semi-empirical method described in Ref. [25] to be -8300.837 kJ/mol. The authors of the title paper have derived accurate high-temperature thermodynamic data for ye'elimite from published vapor pressure results [26]; however, this data is not valid for use at the low temperature required for the theoretical heat calculations and is only used in the phase stability calculations presented later. Data for goethite (FeO(OH)) and gypsum ($CaSO_4$ 2 H_2O) are taken from Ref. [27] and the data for the remaining phases are taken from a thermodynamic dataset recently compiled by Hanein et al. [28]. The major raw materials used in the production of C$A clinker are clay, bauxite, and limestone. Silica is assumed to be introduced as kaolinite ($Al_2Si_2O_5(OH)_4$) and pyrophyllite ($Al_2Si_4O_{10}(OH)_2$). The remaining alumina not furnished as kaolin or pyrophyllite is introduced as gibbsite ($Al(OH)_3$), while all iron is assumed to be introduced as goethite (FeO(OH)). All calcium, except when sulfur is provided as gypsum and/or anhydrite, is assumed to be introduced as calcium carbonate ($CaCO_3$). Conventionally, sulfur is introduced as gypsum and/or anhydrite; however, in this study elemental sulfur and H_2S are also used as surrogates to represent the sulfur content in sulfur-rich fuels.

"Sour" gas and oil or some of their byproducts, e.g. petroleum coke, cannot typically be used as the sole sulfur source in C$A clinker production due to their low sulfur weight content, e.g., crude oil ≤6%w [29] and petroleum coke: ≤6%w [30]. For example, the lower heating value of petroleum coke (30 MJ/kg [31]), when coupled with a typical energy efficiency of 50% [32] results in a maximum attainable concentration of C_4A_3\$ of ≈10% which is too low to provide an acceptable C$A clinker product. There are great advantages in using "sour" oils or their byproducts for the production of C$A clinker at industrial level due to their economic benefits but supplementary sulfur in another form must be added to the fuel. Given adequate information on the available fuels and desired product, a suitable production process can be easily designed.

Current environmental legislation requires that sulfur oxide is not released to the atmosphere in any significant quantity. The pre-heater tower on a modern clinker process will act as an efficient scrubber and provides ample opportunity for additional sulfur uptake by the solids; however, there are benefits to using an additional wet-limestone scrubber on the exiting gas stream. Such a scrubber will produce gypsum which is normally inter-ground with C$A clinker to optimize the cement workability. As well as ensuring that environmental limits are met, this allows additional excess sulfur to be burned to allow additional control over SO_x partial pressures within the kiln/calciner and to generate $CaSO_4$ for inter-grinding. The thermal energy of this excess sulfur combustion is utilized within the kiln, thus our calculations also include the case where 1 mole of $CaSO_4$ per mole of C_4A_3\$ is generated through excess sulfur combustion.

Table 4. A summary of the CO_2 and energy reductions of producing C$A clinker when compared to OPC using four different sources of sulfur. It is assumed that C$A cement is a direct mass-for-mass substitute for OPC.

C_4A_3\$[A] (%w)	Theoretical heat[B] (kJ/kg clinker)	RM-CO_2[C] (%)
Sulfur source: Gypsum		
30	1331	-22.5
40	1326	-28.1
50	1320	-33.7
60	1314	-39.3
70	1309	-44.9
Sulfur source: $CaSO_4$		
30	1322	-22.5
40	1315	-28.1
50	1306	-33.7
60	1298	-39.3
70	1289	-44.9
Sulfur source: Elemental Sulfur		
30	1017 (871)	-18.3
40	908 (713)	-22.6
50	797 (554)	-26.8
60	687 (395)	-31.0
70	577 (237)	-35.3
Sulfur source: H_2S (g)		
30	887 (611)	-18.3
40	734 (366)	-22.6
50	580 (120)	-26.8
60	427 (-126)	-31.0
70	273 (-372)	-35.3

[A]The clinker also contains 10%w C_4AF and β-C_2S as the remainder. The number in parenthesis is the amount of sulfur in the clinker.
[B] The value in parenthesis is the theoretical heat calculated burning excess sulfur to produce 1 mole of anhydrite and/or gypsum for inter-grinding per mole of ye'elimite.
[C] RM-CO_2 savings compared to OPC clinker (CaO in OPC = 67%w [17]).

Under the assumption that C$A cement is a direct mass substitute for OPC, i.e., they can be used for the same applications, and that C$A clinker is defined as containing 30–70% ye'elimite [5], a summary of the environmental impact and energetics of producing C$A clinkers compared to OPC and using four different sources of sulfur is given in Table 4. It is clear that significant CO_2 economies can be achieved through switching to C$A cement, particularly as the products of fuel combustion become a reactive part of the clinker. The theoretical heats of traditional C$A production, where sulfur is provided as gypsum or $CaSO_4$, are significantly higher than when sulfur is combusted. When excess sulfur is combusted and is available as H_2S, the theoretical heats turn negative implying that the production process is exothermic and that fuels are only required to offset heat losses within the kiln. During the desulfurization of fuels, H_2S is generated in large quantities; however, its high toxicity may make its use impractical in a real production process. The use of elemental sulfur is much simpler and still leads to a theoretical heat of 237 kJ/kg, which is just 13% of that of OPC clinker. All formulations presented reduce the CO_2 emissions arising from the calcination of $CaCO_3$ in the raw feed. High-ye'elimite contents achieve a reduction of 45% in emissions when using gypsum or $CaSO_4$, and a 35% reduction when using sulfurous fuels. Although the RM-CO_2 reductions are greater when using gypsum or $CaSO_4$ (assuming gypsum and $CaSO_4$ have no CO_2 burden), it is more advantageous to use sulfurous fuels as the source of sulfur due to their heating value. Overall, combustion of sulfur yields many energetic and environmental advantages. In the next section, the practical feasibility of using sulfur as a fuel source is demonstrated through pilot plant trials.

V. PRODUCTION AT SCALE OF C$A CEMENT VIA SULFUR COMBUSTION

Laboratory experiments for the production of C$A clinkers produced in an air atmosphere do not adequately capture the influence of sulfur within a real process. Generally, small batches of raw materials treated in electrically powered furnaces lose sulfur oxides through partial decomposition of the sulfur-containing phases. In commercial production, it is proposed that the direction of sulfur transfer can be reversed i.e., sulfur is transferred from the gas to the solid phase. Recent experiments by the authors and collaborators in a tube furnace designed to generate controlled atmospheric mixtures of SO_2 and air have demonstrated that the presence of SO_2 in the atmosphere strongly influences the stability of clinker phase composition [33]. These experiments displayed significant SO_3 mass gains in C$A clinker as opposed to more typical mass losses [34]. Hanein et al. [26] recently derived high-temperature

thermodynamic data for ye'elimite from existing vapor pressure data [35] which are combined here with a recently developed thermodynamic database and model [28] to simulate the C$A clinkering process and the solid-gas temperature/partial-pressure stability relationship.

Ye'elimite stability is found to be highly dependent on the temperature and the O_2/SO_2 partial pressures of the kiln atmosphere. Figure 2 displays the results of thermodynamic calculations on the stability of ye'elimite over the valid range of the thermodynamic data, assuming excess SO_2 and O_2 gas compared to the solid phases. The O_2 partial pressure is set at 1% v/v as this approximates the conditions in a conventional industrial kiln [36]. Shaded areas in Figure 2 indicate where ye'elimite is unstable and the dashed lines are used to show the lower and upper limits of SO_2 partial pressures likely to be encountered in conventional kilns [37]. The stability zones in Figure 2 are in agreement with experiments [19, 33] and demonstrate that it is essential to control both operating temperatures and the system atmosphere in order to optimize production of ye'elimite. When considering all phases which are likely to form in C$A, narrower bounds on the operating conditions which allow for the production of C$A clinker are derived through computation. This approach was used in the development of the production process [24] trialed at pilot scale [20]. The kiln used was 7.2 meters in length and the dry raw meal feed rate was ≈25 kg/hr; target clinkers were produced using elemental sulfur both as a fuel and as the source of "SO_3". The clinkers were sintered at 1261 ±13°C as measured by optical pyrometry [20]. Target, measured, and thermodynamically predicted phase compositions of the produced clinkers are shown in Table 5. Due to lack of thermodynamic data for some phases at that time, only the kiln atmosphere was designed thermodynamically pre-trial. Clinker phase formulation was designed using stoichiometric assumptions and that the stable ferrite composition would be C_6A_2F; later work has shown that its composition lies close to C_4AF: this composition will be used in subsequent iterations [20]. After the trial, thermodynamic predictions were developed and compared with the phase contents actually achieved as determined by XRD Rietveld measurements. Where differences occurred they can be ascribed to delineate kinetic aspects, e.g., the sluggish kinetics leading to slow transformation of gehlenite, C_2AS, to belite and ye'elimite. At the time of writing this work, the thermodynamic model is being used to design a second set of pilot scale trials scheduled for mid-February 2016.
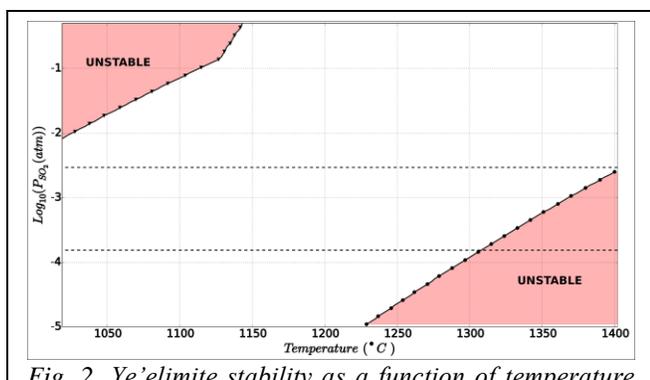
Fig. 2. Ye'elimite stability as a function of temperature and SO$_2$ partial pressure calculated for a constant partial O$_2$ pressure equivalent to 1 %v. Ye'elimite is stable within the clear field. Dashed horizontal lines show conditions likely to be obtained in commercial kilns thus further restricting favorable conditions for forming ye'elimite.

Table 5. Comparison between the target, measured, and thermodynamically predicted clinker phase compositions.

	Clinker phase (%w)					
	C$_4$A$_3$$	C$_2$S	C$_6$A$_2$F	C$_4$AF	C$	C$_2$AS
Stoichiometric target [20]	40	47	11	…	…	…
QXRD measurements [20]	36	43	…	2	10	5
Thermodynamic predictions	43	43	…	7	…	…

The produced clinkers are currently undergoing mechanical and physical testing at the University of Aberdeen. In the pilot trial [20], the sulfur in the kiln exit gas not captured by the clinker batch was scrubbed using sodium bicarbonate as an absorbent as the low thermal efficiency of the kiln used (3%) required significant fuel and therefore excess sulfur combustion to maintain SO$_x$ partial pressures. The upper limit of C$A clinker phase stability in SO$_2$ partial pressure should not, in practice, limit the amount of sulfur which can be combusted in the production of C$A clinker as the sulfur can be burned in more than one zone, e.g., in the pre-calciner which is a ubiquitous fixture in conventional kilns, effectively generating CaSO$_4$.

Although Figure 2 indicates a large window of stability of ye'elimite, even at very high partial pressures of SO$_2$, care must be taken when designing the clinker process and formulation as other possible phases must be considered in the thermodynamic calculations. For example, in the case in Table 4 where 100% H$_2$S is suggested as a fuel, it is calculated thermodynamically that the clinkering temperature must be greater than 1330°C as below this temperature, C$_2$AS and C$ are stable over C$_2$S and C$_4$A$_3$$ under the specified conditions. These conditions may prove impractical to achieve; although the significant reductions in CO$_2$ may warrant further investigation.

VI. CONCLUSION

It is shown here that utilizing fuel combustion products to form reactive cement clinker phases is highly effective in significantly reducing the environmental effects caused by the production of cement. The operating conditions, feasibility, and economics of the process can be optimized quickly using computational thermodynamics; as a result, the pace of the changes required to meet the CO$_2$ emissions and sustainability demands on the cement industry can be accelerated.

A novel process technology for the production of C$A cement is used as an example and it is shown that applying this technology can greatly reduce specific CO$_2$ emissions in the cement industry. The technology suggested here surpasses the 2030 CO$_2$ reduction target (25–30%) of the Low Carbon Technology Partnership initiative for the cement industry [3]. This is achieved by producing C$A cement as an alternative to OPC using sulfur combustion. The combustion product of sulfur is sequestered as an integral part of the clinker and its inter-ground products. The process has been demonstrated in kilns designed for OPC production, thus existing plant technology can be utilized. Of course, the handling of raw feed and products is somewhat different but this requires minimal adjustments to existing equipment. The application of thermodynamic calculations to model the key reactions and to optimize the process has led not only to new understanding but also greatly shortened the time required to provide a technological basis for new low carbon cements.

VII. ACKNOWLEDGEMENTS

REFERENCES

[1] (2009). *World Business Council for Sustainable Development, The cement Sustainability initiative: "Getting the Numbers Right", Cement Industry Energy and CO2 Performance.* Available: http://www.wbcsdcement.org/pdf/CSI%20GNR%20Report%20final_updated%20Nov11_LR.pdf

[2] (2009). *World Business Council for Sustainable Development, Cement Technology Roadmap 2009: Carbon emissions reductions up to 2050.* Available: http://www.wbcsdcement.org/pdf/technology/WBCSD-IEA_Cement%20Roadmap.pdf

[3] (2015). *World Business Council for Sustainable Development, "Low Carbon Technology Partnerships initiative": Cement.* Available: http://lctpi.wbcsdservers.org/wp-content/uploads/2015/12/LCTPi-Cement-Report.pdf

[4] M. Schneider, M. Romer, M. Tschudin, and H. Bolio, "Sustainable cement production—present and future," *Cement and Concrete Research,* vol. 41, pp. 642-650, 2011.

[5] M. C. G. Juenger, F. Winnefeld, J. L. Provis, and J. H. Ideker, "Advances in alternative cementitious binders," *Cement and concrete research,* vol. 41, pp. 1232-1243, 2011.

[6] A. Hasanbeigi, L. Price, and E. Lin, "Emerging energy-efficiency and CO2 emission-reduction technologies for cement and concrete production: A technical review," *Renewable and Sustainable Energy Reviews,* vol. 16, pp. 6220-6238, 10// 2012.

[7] W. Dienemann, D. Schmitt, and F. Bullerjahn, "Belite-Calciumsulfoaluminate-Ternesite (BCT)-a new low carbon clinker technology," *Cement International,* vol. 11, pp. 100-109, 2013.

[8] Q. Zhou, N. B. Milestone, and M. Hayes, "An alternative to Portland Cement for waste encapsulation—The calcium sulfoaluminate cement system," *Journal of Hazardous Materials,* vol. 136, pp. 120-129, 8/10/ 2006.

[9] F. P. Glasser and L. Zhang, "High-performance cement matrices based on calcium sulfoaluminate–belite compositions," *Cement and Concrete Research,* vol. 31, pp. 1881-1886, 12// 2001.

[10] I. Chen and M. Juenger, "Synthesis and hydration of calcium sulfoaluminate-belite cements with varied phase compositions," *Journal of Materials Science,* vol. 46, pp. 2568-2577, 2011.

[11] "Rapid Hardening sulphoaluminate Cement," vol. JC 714-1996, ed: Professional Standard of Building Materials Industry of People's Republic of China. State Administration of Building Materials Industry, 1997.

[12] E. Gartner, "Industrially interesting approaches to "low-CO2" cements," *Cement and Concrete Research,* vol. 34, pp. 1489-1498, 9// 2004.

[13] S. Ma, X. Shen, Y. Huang, and B. Zhong, "Preparation and formation mechanism of calcium sulphoaluminate," *Chinese ceramic society,* vol. 36, p. 78, 2008.

[14] P. K. Mehta, "Investigations on energy-saving cements," *World cement technology,* vol. 11, pp. 166-177, 1980.

[15] *Commercial CSA cement.* Available: http://www.chngn.com/product_show.asp?id=1659&class_id=298

[16] F. Bullerjahn, M. Zajac, and M. B. Haha, "CSA raw mix design: effect on clinker formation and reactivity," *Materials and Structures,* pp. 1-17, 2015.

[17] H. F. W. Taylor, "Cement chemistry," *Telford, London,* 1997.

[18] S. Jewell and S. M. Kimball. (2015). *Mineral Commodity Summaries 2015.* Available: http://minerals.usgs.gov/minerals/pubs/mcs/2015/mcs2015.pdf

[19] J. Strigac and J. Majling, "Phase composition development of calcium sulphoaluminate belite cement in the SOx atmosphere," *World cement,* vol. 28, pp. 97-98, 1997.

[20] T. Hanein, I. Galan, A. Elhoweris, S. Khare, S. Skalamprinos, G. Jen*, et al.*, "Production of Calcium SulfoAluminate cement using sulfur as a fuel and as a clinker sulfur trioxide component source: Pilot kiln trial," U. o. Aberdeen, Ed., ed. Unpublished manuscript, 2016.

[21] H. Bolio-Arceo and F. P. Glasser, "Formation of spurrite, Ca5(SiO4)2CO3," *Cement and Concrete Research,* vol. 20, pp. 301-307, 1990.

[22] *United States Geological Survey: Minerals Information.* Available: http://minerals.usgs.gov/minerals/pubs/commodity/sulfur/

[23] R. Bacon and S. Tordo, "Crude oil price differentials and differences in oil qualities: a statistical analysis," *World Bank,* 2005.

[24] M. Imbabi, F. P. Glasser, and I. Galan, "A method for producing cement-WO2014/177858A8," 2014.

[25] A. T. M. G. Mostafa, J. M. Eakman, and S. L. Yarbro, "Prediction of standard heats and Gibbs free energies of formation of solid inorganic salts from group contributions," *Industrial & engineering chemistry research,* vol. 34, pp. 4577-4582, 1995.

[26] T. Hanein, A. Elhoweris, I. Galan, F. P. Glasser, and M. N. Campbell Bannerman, "Thermodynamic data of ye'elemite (C4A3S) for cement clinker equilibrium calculations," in *35th Cement & Concrete Science Conference.*, Aberdeen, 2015.

[27] D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, and I. Halow, "The NBS tables of chemical thermodynamic properties. Selected

values for inorganic and C1 and C2 organic substances in SI units," DTIC Document1982.

[28] T. Hanein, F. P. Glasser, and M. Bannerman, "Thermodynamics of Portland Cement Clinkering.," in *14th International Congress on the Chemistry of Cement.*, Beijing, China, 2015.

[29] W. L. Orr, "Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation--study of Big Horn basin Paleozoic oils," *AAPG bulletin,* vol. 58, pp. 2295-2318, 1974.

[30] J. M. Lee, J. J. Baker, J. G. Rolle, and R. Lierena, "Comparison of fuel properties of petroleum cokes and coals used in power generation," 1999, pp. U810-U810.

[31] B. Boundy, S. W. Diegel, L. Wright, and S. C. Davis, "Biomass Energy Data Book, US Dep. Of Energy, 2011," *ORNL/TM-2011/446, http://cta.ornl.gov/bedb/download.shtml*

[32] K. E. Peray and J. J. Waddell, *The rotary cement kiln*. London, United Kingdom: Chemical Publishing Company, 1986.

[33] I. Galan, A. Elhoweris, T. Hanein, M. N. Campbell Bannerman, and F. P. Glasser, "Advances in clinkering technology of calcium sulfoaluminate cements," U. o. Aberdeen, Ed., ed. Unpublished manuscript, 2015.

[34] N. Ukrainczyk, N. Frankoviæ Mihelj, and J. Šipušić, "Calcium Sulfoaluminate Eco-Cement from Industrial Waste," *Chemical and Biochemical Engineering Quarterly,* vol. 27, pp. 83-93, 2013.

[35] G.-S. Choi and F. P. Glasser, "The sulphur cycle in cement kilns: Vapour pressures and solid-phase stability of the sulphate phases," *Cement and Concrete Research,* vol. 18, pp. 367-374, 5// 1988.

[36] T. I. Barry and F. P. Glasser, "Calculations of Portland cement clinkering reactions," *Advances in cement research,* vol. 12, pp. 19-28, 2000.

[37] U. Kääntee, R. Zevenhoven, R. Backman, and M. Hupa, "Cement manufacturing using alternative fuels and the advantages of process modelling," *Fuel Processing Technology,* vol. 85, pp. 293-301, 3/15/ 2004.