Carbon footprint of calcium sulfoaluminate clinker production

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ABSTRACT

Novel cement formulations based on calcium sulfoaluminate clinkers have significantly lower carbon dioxide emissions during production when compared against conventional Portland cement; however, there are no systematic studies of the environmental impact associated in producing these formulations. Previous studies are limited to qualitative evidence that emissions are lower due to a combination of favourable thermodynamics and a reduced usage of limestone. This work evaluates the eco-efficiency of calcium sulfoaluminate clinker production through an analysis of the carbon footprint and costs over the entire clinker production process (cradle-to-gate). Several sulfur sources are considered including calcium sulfate, as both gypsum and anhydrite, and a novel solid-sulfur combustion process in kilns. This latter process has the added advantage of reducing the fuel demand required to reach clinkering temperatures during the manufacturing process. The analysis demonstrates an overall reduction of emissions of 25–35%, which varies largely as a function of the phase composition of the final clinker but is almost independent of the sulfur source. The high aluminium oxide content in the final calcium sulfoaluminate clinker formulation requires the use of alternative raw materials and by-products from the aluminium industry such as high-alumina clays, alumina-rich wastes, or bauxite. Bauxite, which is only abundant in specific regions of the world, is detrimental to the economics of calcium sulfoaluminate clinker production. Despite this, costs of the clinker production remain competitive and the process displays significant potential for improving the environmental impact of cement production.

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1. Introduction

Each year approximately 4 billion tonnes of Portland cement (PC) are produced globally (Jewell and Kimball, 2015). Due to the high demand for PC, its production emits on average 0.87 tonnes CO_2e (equivalent carbon dioxide) per tonne of cement (Damtoft et al., 2008) and these emissions are a considerable fraction of the overall greenhouse gas (GHG) emissions from human activity. The total CO_2 emissions from cement manufacture comprise 8% of global emissions (Olivier et al., 2016). To reduce these emissions, the cement industry has prioritised four key avenues of research: (1) the use of alternative raw materials and fuels, (2) the use of substitute and supplementary cementitious materials (SCM), (3) carbon dioxide capture and sequestration, and (4) the formulation of alternative low-carbon binders. Each of these avenues has its own challenges and advantages.

The adoption of alternative raw materials/fuels and the use of SCMs have already been applied by the industry as it has been a relatively straightforward and incremental change; however, it is well known that their capacity for improvement is limited (Gartner and Hirao, 2015). The current levels of alternative fuel consumption have shown no impact on GHG emissions from cement kilns and their use is more often related to improving the economic performance of the process than its environmental performance (Galvez-Martos and Schoenberger, 2014). Carbon dioxide capture and sequestration is unattractive to cement manufacturers as it requires major investments in plant equipment to perform the capture (Schneider, 2015) and is currently uneconomical without supporting regulation schemes to incentivise its adoption.

Market uptake of novel formulations of cement binders to be used in general construction applications is hindered by the lack of standardisation, which in turn delays the subsequent use of these new binders by the construction industry. However, "new" binders can bring mid-term emissions reductions without any major disruptive changes or the requirement of large capital investment in plant redesign (World Business Council for Sustainable

Abbreviations

CO_2e	Equivalent CO_2 emissions
C$A	Calcium SulfoAluminate
ELCD	European Life Cycle Database
GHG	Greenhouse gases
IAI	International Aluminium Institute
OPEX	Operational expenses
PC	Portland cement
STP	Standard temperature and pressure
Tkm	Tonne-kilometre
USGS	United States Geological Survey
XRF	X-ray fluorescence

Development, 2009a). Amongst the alternative binders proposed so far, calcium sulfoaluminate (C$A) cements containing significant fractions of ye'elimite are particularly promising (Juenger et al., 2011). C$A cements require less calcium per tonne than PC thus the amount of CO_2 released through the calcination of calcium carbonates in limestone, chalk, and marble is reduced (Gartner, 2004; Quillin, 2009). The manufacture of C$A still utilizes a kiln process; however, the process efficiency is improved when compared to PC production due to the more favourable theoretical heat requirements of C$A compositions (Hanein et al., 2016a). Gartner, 2004, identified C$A cements as low carbon cements suited for specialized applications with high early strength requirements; also, as an additive to other binders to control shrinkage or expansion; however, optimised compositions of C$A can also provide a similar performance to PC with a potentially significant reduction in GHG emissions if used as mass for mass substitute. The high fraction of bauxite typically required in the raw meal makes C$A cements relatively more expensive than Portland cement (Juenger et al., 2011); however, it has been proven that an economically-optimised composition can be achieved with high alumina clays (Hanein et al., 2016b) or even Al_2O_3-rich wastes (Gartner and Hirao, 2015).

Due to the enormous scale of cement production, careful consideration must be given to the abundance of the raw materials for any new formulation. The raw materials for C$A cement manufacture differ from those used for PC. The C$A clinkering process requires a source of sulfur which can be supplied as calcium sulfate, i.e. gypsum or anhydrite, which are naturally sourced (mined) or recovered from waste (e.g. from flue gas desulfurisation) or raw sulfur, which can be burnt as a fuel (Hanein et al., 2016b). The annual world production of elemental sulfur is 72.4 Mt/yr (Jewell and Kimball, 2015) 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. Apart from being readily available to locations near oil and gas refineries, elemental sulfur can also be found and mined near hot springs and volcanic regions in many parts of the world and is well distributed geographically. Current annual elemental sulfur production is sufficient to produce ≈3500 Mt/yr of a C$A clinker of 40% ye'elimite which is almost equivalent to the current world demand for cement; thus, the availability of sulfur would not be concern if C$A cements were adopted in mass. Depending on the final formulation, sources of bauxite may also be required due to the higher need for aluminium oxide in calcium sulfoaluminate cements which cannot normally be provided from clays and/or shales only. This appears to be the key limitation in the commercial production of C$A clinkers (Gartner and Hirao, 2015); however, other limitations may also appear due

to the higher demand of gypsum for C$A clinkers manufacturing.

Although it has generally been stated that C$A cements have a lower associated carbon footprint, no systematic scientific study on the real influence of the clinker composition and the raw material supply chain on the associated global warming potential and economics of C$A cement production exists in the literature. This paper aims to explore these aspects of C$A manufacture in a cradle-to-gate assessment (i.e., from raw material to the final product leaving the factory gate) using a simplified Life Cycle Assessment (LCA) methodology looking only at the carbon footprint. A preliminary evaluation of the economics of C$A manufacture is also performed by evaluating relative marginal costs changes. The aim is to obtain a quantitative understanding of the environmental hotspots and trade-offs of C$A formulations. A particular novelty of the current work is the evaluation of the use of sulfur as fuel and raw material, as proposed by Hanein et al. (2016b), compared to the more conventional use of calcium sulfate (gypsum or anhydrite).

2. System definition, data sources, and assumptions

2.1. Goal, scope, and functional unit

A simplified LCA methodology is used for the evaluation of life cycle GHG emissions in the production of various C$A clinker compositions and a standard PC clinker (control). The objective is to benchmark C$A formulations against conventional PC and to analyse the sensitivity of the results through the parametric variation of the energy and mass balances. The study will focus on the production process of clinker from raw materials, i.e. cradle-to-gate. The analysis includes the life cycle of the raw materials and for simplicity it excludes refinement processes such as blending or grinding used to produce the final cement; however, it includes the benefits achieved from the use of by-products. Data are taken from various sources from western economies: specific data are taken from the life cycle inventory of aluminium from United States' studies (e.g. The Aluminium European Aluminium Association, 2013), while some are taken from world averages (e.g. IEA, 2008). From the perspective of this study this approach is acceptable as the objective is to evaluate the relative variation of emissions without a specific focus on a production or mining facility.

It is common practice that when comparing products the basis of the calculation, i.e. the functional unit in LCA terminology, corresponds to the amount or value of a product that provides the same service or function. This implies that the same functionality of each analysed clinker should be compared rather than a fixed quantity; however, a final use (e.g. civil construction) or final product (e.g. a concrete block) is difficult to define for two types of cements due to the diverse applications, the different mineralogy, and the performance of the final formulation of the cement in terms of strength and durability. The functionality of C$A cements, regarding these issues, is not yet well developed and standardisation of C$A products is yet to be achieved in the western world. The problem with the characterisation of a functional unit for different cement formulations can be well understood through the clinker factor, which is the ratio of clinker in the final cement. The clinker factor is on average 0.90 for PC but can be lower than 0.5 if cementitious wastes or SCMs such as pulverised fly ash, silica fume, or ground granulated blast-furnace slag, are added to the final product; the use of SCMs is one of the key GHG reduction potentials of PC manufacture (Boesch and Hellweg, 2010). The same is observed with cement mineralogy; currently, lower content ye'elimite and higher content reactive belite clinkers called BYF (belite-ye'elimite-ferrite) have been developed to reduce the use of bauxite in the raw meal and improve the performance of the cement (Gartner and Sui, 2017).

Unfortunately, comparable cement formulations of C$A and PC are rather limited by the type of additions, their mineralogy, and their environmental performance which depends on the inherent properties of the final products. For instance, the clinker factor of C$A cements is difficult to state in general as it is a type of clinker that can be used with almost no addition to the clinker or with rather low additions of other materials as gypsum (Beltagui et al., 2017). It is fair to say that C$A products are still not well understood and the optimisation towards competitive commercial C$A products is still limited. For instance, C$A formulations including fly ash are found to be reliable (Garcia-Mate et al., 2013) but large-scale application is yet to be attempted. Due to the aforementioned reasons, and to facilitate the benchmarking of production processes rather than products, this study compares emissions and costs per tonne of *clinker*. The results of this work may be considered for the calculation of the environmental impact of cement-based products; but, any use of the results must consider the implications of the assumptions made.

2.2. Methodology

Carbon dioxide is the main culprit of the so-called greenhouse effect. Prior to the industrial revolution; atmospheric CO_2 concentrations were fairly stable at 280 ppm but today are around 400 ppm. Other anthropogenic emissions also have a considerable environmental effect, e.g. methane, nitrous oxide, and fluorinated gases; the effect of these other gases is often accounted for as an equivalent mass of CO_2 which produces the same effect, i.e. equivalent CO_2 or CO_2e. As each gas is active over different time-scales, the CO_2e calculated in this document uses effects within 100 years as a basis in line with the approach of the Intergovernmental Panel on Climate Change (Simmons, 2007). The use of mass of CO_2e as a measure of the greenhouse effect is also quite well known as the Global Warming Potential, GWP, in the field of LCA. The amount of equivalent emissions per tonne is known as the emission factor, carbon intensity or carbon footprint.

Using this methodology, the emissions from the supply chain of raw materials consider the whole amount of equivalent CO_2, including e.g. 21 kg CO_2e per kg of methane, or 298 kgCO_2e per kg of N_2O. However, the operational emissions balance of clinker production only considers real CO_2 emissions from the internal processes such as combustion and calcination.

The GWP is calculated using an *attributional* approach, i.e., environmental pressures are associated to every mass and energy input or output of the process. This methodology assumes that there are no relevant changes in the impacts arising from the supply chain due to the production of a new product. This is opposed to *consequential* analyses, where the influence of the new process, product, or service is calculated according to certain economic equilibrium rules. For instance, manufacturing C$A cement at global scale would certainly affect the economy of bauxite, high alumina clays, and/or alumina-bearing wastes, and of course impact on their logistics and thus the environment. For simplicity, this is not considered in this work and, to validate the applicability of the results of this study, further research will be required if C$A manufacture is adopted at scale.

As discussed in the following sections, in this work where a choice is available in the approximations used (such as fuel type, inclusion of secondary processing, etc.) the choices are made to favour PC manufacture in order to ensure that a conservative estimate of the benefits of C$A manufacturing is conducted.

2.3. Product system

Our product system is defined as the set of processes required to produce the assessed clinkers from raw materials, this includes: extraction, preparation, transport, and chemical transformations with an influence on the mass and energy balance. Due to an assumed higher relative importance of raw materials in the production of C$A clinkers than for PC, a special emphasis in the description of the formulation is presented below.

Chemically, the primary difference between C$A and PC clinkers is their mineralogy; C$A contains ye'elimite, ($C_4A_3\$$), rather than alite (C_3S) as a major constituent (Juenger et al., 2011). Both clinkers contain belite (C_2S) and ferrite ($C_2(A,F)$); N.B. for simplicity, all cement clinker phases are expressed using the oxide notation outlined in Table 1, using $ to refer to SO_3. The raw feed used in the conventional manufacture of cement contains oxides of calcium, silicon, aluminium and iron, plus other minor components that are usually supplied from readily-available low-cost sources; calcium oxide is the major/key component. Limestone, composed primarily of $CaCO_3$, is generally the main source of calcium for all cement manufacturers (chalk and marble may also be used) and has a significant effect on the GHG emissions as it needs to be calcined into lime (CaO) and CO_2 through high temperature treatment. The remaining ingredients required for the raw mix are usually supplied from siliceous clays, shales, and/or fly ash. The substantially lower lime factor in the mineralogy of C$A reduces the amount of limestone needed when compared to PC, but brings about an increase in the amount of alumina and sulfur oxides required in the raw meal. Alumina-rich clays have already proven to be effective (Hanein et al., 2016b) as substitute of the more conventional bauxite. Industrial by-products such as slag have also been successfully utilized as an alumina source (Whittaker et al., 2014); however, alumina sources are scattered in their global distribution and carry higher burdens of CO_2e emissions due to higher needs of transport and distribution (IEA, 2008).

To produce the clinkers for both types of cement (PC and C$A), the raw materials are sintered using fuels such as pet coke, coal, and waste-derived fuels that provide the necessary heat and temperature required to produce clinker with a specific phase assemblage. The use of coal or pet coke is associated with high CO_2 emissions while waste-derived fuels, although allowing for a better economic performance of the process, do not produce a statistically significant reduction in emissions (Galvez-Martos and Schoenberger, 2014). Elemental sulfur is a by-product which arises from the Claus process employed during the desulfurization of sulfur-rich (sour) oil and gas; it is therefore readily available. It has already been demonstrated that the products of sulfur combustion, sulfur dioxide and oxygen, are readily transferred from the gas phase to the solids to form clinker phases such as ye'elimite (Strigac and Majling, 1997). Of course, the combustion of sulfur does not produce CO_2; however, the following must be considered:

- Although sulfur is a by-product, it has a relatively healthy demand, e.g. to produce sulfuric acid, and it also has a non-negligible price around EUR 90–100 per tonne (Jewell and Kimball, 2015). Therefore, it is not considered a waste and any LCA where sulfur is an input should consider emissions from its production process. According to the European Commission ELCD database, emissions from sulfur production are 489 kg CO_2e per tonne; this value is used in this work.
- The combustion of excess sulfur (to that incorporated in the clinker) is required due to chemical equilibrium constraints and

Table 1
Cements oxides notation used in this work.

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

produces excess SO_x gas at the exhaust of the kiln. Due to the negative environmental impact of this gas, these emissions must be abated by reaction with calcium oxide and oxygen to produce solid calcium sulfate, most probably via the more efficient wet process. This simple process has a non-negligible carbon footprint as CO_2 is produced in the calcination of limestone to produce the CaO that is used as the absorbent. At the same time, the produced calcium sulfate can substitute the natural gypsum used as an inter-grinding additive in the manufacture of cement from clinker. These emission trade-offs are considered in this study.

Under the constraints outlined so far, a simplified flowchart of the process can be constructed as in Fig. 1. The figure distinguishes between those emissions associated to operations and processes occurring in the kiln (operational emissions) and those associated with the raw materials input into the kiln – from mining to transport and distribution (supply chain emissions).

2.4. Assumptions

As stated earlier, this analysis is conducted using a cradle-to-gate approach of the production of C$A clinker. The generic equation below outlines the main contributions to the GHG emissions from C$A clinker production:

accurately predicted from a set of six parameters, as defined by Ammenberg et al. (2011) and corroborated by Galvez-Martos and Schoenberger (2014): (1) clinker factor, (2) CO_2 emissions from calcination, (3) final energy consumption (as fuel) (4) share of cleaner fuels (e.g. from biogenic sources), (5) specific electrical energy consumption, and (6) share of renewable electricity. The impact from the post-production phase, e.g. electricity consumption in the clinker grinding process, is excluded as it is assumed to be similar to that of PC clinkers; however, studies have shown that C$A clinker is easier to grind than PC clinker thus it is likely that this assumption favours PC (Schneider, 2015).

The most prominent emission impacts will arise from the calcination of limestone and the combustion of fuels. Part of the limestone is replaced with other raw materials in C$A clinker when compared to PC clinker. Consequently, the major focus of this study is the analysis of the overall trade-off from reduced limestone calcination, lower theoretical energy requirements, and higher emissions from the supply chain of additional raw materials such as the source of sulfur and bauxite.

To design the various raw mixtures, the compositions of the clay, limestone, gypsum, and bauxite used in this work are obtained from the raw materials used in the previous pilot-scale trials (Hanein et al., 2016b; 2017) as X-ray Fluorescence (XRF) analysis of their composition is available and they are representative of the raw products commercially available in large volumes: limestone
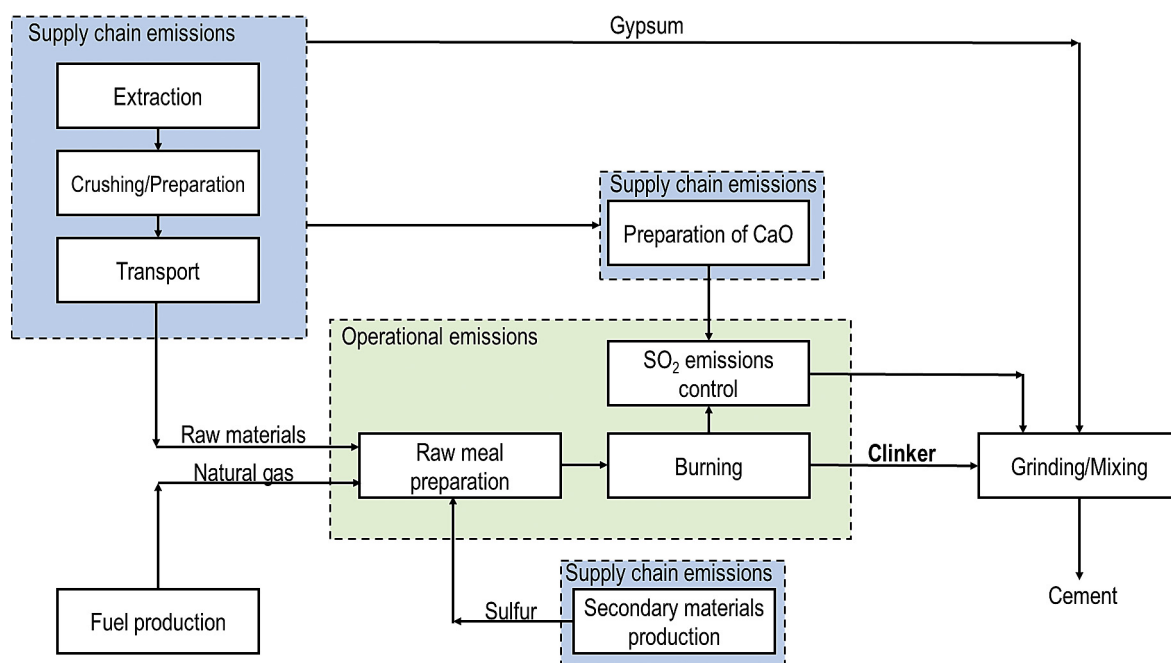
$$\{\text{emissions from C\$A clinker production}\} \approx \{\text{emissions from } CaCO_3 \text{ calcination}\} + \{\text{emissions from fuel combustion}\} + \{\text{emissions from the supply chain of materials}\} \tag{1}$$

Equation (1) is a simplification of the full emissions balance as many secondary processes also have associated emissions; however, most of the CO_2e emissions from cement production can be

(Samin, France), clay (Zhengzhou Haixu abrasives, China), bauxite (Zhengzhou Haixu abrasives, China), and gypsum (Saint-Gobain, United Kingdom). The oxide composition of the limestone and

Fig. 1. Clinker system flowchart used for the calculation of life cycle assessment greenhouse gases emissions.

Table 2
Oxide composition of the raw materials used to derive raw mix designs for this work (wt. %).

	CaO	Al$_2$O$_3$	SiO$_2$	Fe$_2$O$_3$	TiO$_2$	MgO	K$_2$O	Na$_2$O	SO$_3$
Limestone	55.7	–	0.1	0.009	–	0.26	–	–	–
Bauxite	0.16	69.32	11.52	1.21	3.409	0.0	0.455	–	–
Clay	0.87	38.18	39.24	5.98	1.773	0.06	0.624	–	–
Gypsum	37.69	0.12	1.08	0.04	0.01	0.87	0.03	0.02	50.51

gypsum were provided by the respective suppliers. As economical cement production must use local mineral sources which can have significant variation in composition depending on the location of the plant, the results presented here do not immediately generalise to production everywhere but provide an illustrative example. Anhydrite is assumed here to be pure CaSO$_4$. The major oxide compositions of the raw materials are shown in Table 2.

The composition of the theoretical raw meal is calculated for C$A clinker outputs containing between 30 and 70% ye'elimite, 10% ferrite (C$_4$AF), and the remaining as belite. A constrained optimisation is performed to minimise the amount of bauxite required (to allow favourable economics) while meeting the minimum ye'elimite content requirements and ensuring no free lime or anhydrite is present in the system (which are undesirable products). The ferrite content is unconstrained and varies between 2 and 10%. The assumptions made for the raw material calculations include the following: (1) all alkali react to form alkali sulfates, (2) all TiO$_2$ react to form CaTiO$_3$, (3) all silica react to form belite, (4) all iron reacts to form ferrite (C$_4$AF), (5) MgO is unreactive, and (6) no sulfur is lost during pyro-processing. For each formulation, the calculated compositions of raw materials are shown in Table 3. It should be noted that the actual C$A clinker output does not only depend on the raw mix but also on the conditions in the clinkering zone including temperature and SO$_2$ and O$_2$ partial pressure (Hanein et al., 2017). For simplicity, it is assumed that the kiln is operated such that the conditions within the kiln are appropriate for C$A manufacture without considering the operational challenges this implies in maintaining an adequate SO$_2$ atmosphere.

For the theoretical heat calculations, silica is assumed to be introduced as kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) and pyrophyllite (Al$_2$Si$_4$O$_{10}$(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 is assumed to be introduced as calcium carbonate (CaCO$_3$) except for any that is present in gypsum and/or anhydrite when they are used. Thus, the theoretical heat demand of the kiln process is calculated from the change in the enthalpy content from the raw materials to the final product. The reference heat of formation at STP of ye'elimite is taken to be −8406.493 kJ/mol (Costa et al., 1972). Data for goethite (FeO(OH)) and gypsum (CaSO$_4$.2H$_2$O) are taken from Wagman et al. (1982), and the data for the remaining phases are taken from a thermodynamic dataset recently compiled by Hanein et al. (2015). The total heat demand of the kiln process is thus the sum of the theoretical heat plus an assumed fixed heat loss taken from the PC manufacturing kiln processes which is 2 GJ per tonne of clinker (calculated from World Business Council for Sustainable Development, 2009b). A deeper analysis of the thermal efficiency of the kiln is required to take into account heat loss variations (compared to PC) brought about by the lower temperature required for C$A clinker manufacture, the associated change of gas flow, changes in chemical composition, and the different thermal behaviour at the low temperature end of the gas exhaust. Due to the lack of information on the performance of C$A kilns, the average thermal loss from PC clinker manufacturing, 2 GJ, has been assumed for C$A clinkers.

In this work, the effects of three sulfur sources are assessed: (1) calcium sulfate dihydrate (gypsum), (2) calcium sulfate (anhydrite) and (3) elemental sulfur. Two cases of elemental sulfur are used; stoichiometric combustion of sulfur and 100% excess of stoichiometric sulfur combustion. The excess sulfur can be scrubbed from kiln flue gas to produce gypsum that can potentially be utilized for inter-grinding with clinker, but which will increase investment costs. This range of excess sulfur is used as it covers the likely operating ranges required in full-scale production and facilitates an investigation on the economics of the sulfur combustion approach. These four scenarios, along with PC, are summarised in Table 3. The input raw materials and fuel data from Chen et al. (2010), are taken as the benchmark values for PC. In this case, only clay and limestone are considered as the main contributors to the environmental burden and cost of PC.

Natural gas is used here as the fuel source; however, other fuels such as coal or solid residue fuel are also frequently combusted in

Table 3
Raw materials and theoretical heat from fossil fuel for the different assessed scenarios.

Source of sulfur	Target formulation C$_4$A$_3$$ (%w)	Clay (%w)	Limestone (%w)	Bauxite (%w)	Gypsum/ Anhydrite (%w)	kg raw material/ kg clinker	Theoretical heat (kJ/kg clinker)
Gypsum	30	33.9	60.5	–	5.6	1.46	1279
	40	26.9	57.4	8.4	7.3	1.44	1256
	50	19.4	54.1	17.2	9.3	1.42	1234
	60	11.7	50.7	26.4	11.3	1.40	1211
	70	3.7	47.1	35.8	13.4	1.38	1188
CaSO$_4$	30	34.2	60.9	–	4.9	1.46	1270
	40	27.4	58.0	8.3	6.3	1.43	1245
	50	19.9	54.8	17.3	8.0	1.41	1220
	60	12.2	51.5	26.5	9.8	1.39	1194
	70	4.2	48.1	36.0	11.6	1.37	1168
Elemental Sulfur	30	34.7	65.3	–	–	1.50	965
	40	27.8	63.7	8.5	–	1.49	838
	50	20.3	62.0	17.6	–	1.48	711
	60	12.5	60.3	27.1	–	1.47	583
	70	4.3	58.5	37.2	–	1.46	456
100% Excess Sulfur	30	34.7	65.3	–	–	1.50	819
	40	27.8	63.7	8.5	–	1.49	644
	50	20.3	62.0	17.6	–	1.48	468
	60	12.5	60.3	27.1	–	1.47	292
	70	4.3	58.5	37.2	–	1.46	116
PC	0	19	81	–	–	1.66	1780

Table 4
Assumptions, emissions factors and carbon intensities for the calculation of the GHG balance of C\$A clinker production.

Parameter	Value	Unit	Reference
Kiln heat losses	2	GJ/tonne of clinker	Assumed in this work
LHV Natural Gas	35.1	MJ/m^3	Eurogas, 2013
Heat from sulfur combustion	9.278	MJ/kg	Eckman and Rossini, 1929
Emission factor, natural gas combustion	0.056	kg CO_2e/MJ	U.S. EIA, 2016
Emission factor, supply of limestone	38	kg CO_2e/tonne	ELCD, 2006a
Emission factor, supply of sulfur	489		ELCD, 2006b
Emission factor, supply of gypsum/anhydrite	50		Fisher, 2008.
Emission factor bauxite, mining (a)	11		European Aluminium Association, 2013
Emission factor bauxite, transport (b)	62		The Aluminum Association, 2013; International Energy Agency, 2008; McKinnon, 2007
Emission factor, supply of bauxite (a) + (b)	140		Calculated
Emission factor, supply of clay,	3.7		Koroneos and Dompros, 2007.

cement making. The lack of experience of alternative fuels with C\$A and the harmonisation required on the assessment to evaluate the influence of the introduction of sulfur are the two main reasons behind this approximation. Both issues needed to be solved, from a mass and energy balance perspective, by assuming the same fuel for both C\$A and PC clinkers, so that the influence of other parameters of the product system could be isolated. In fact, it is expected that waste-derived fuel or pet coke will be richer in sulfur, which would in turn favour the formation of C\$A cements. As C\$A also has a lower heat demand than PC, the use of natural gas leads to a conservative estimate of the reduction in fuel derived CO_2 emissions when compared to PC. Another reason to exclude "usual" fuel mixes is the uncertainty of the GHG balance (Galvez-Martos and Schoenberger, 2014) when considering wastes and solid residue fuels. These fuels tend to produce economic savings but the impact on emissions, although often claimed to be positive, has little statistical significance. By simplifying the fuel to natural gas, a common emissions basis can also consider the fuel economy of the kiln and remove the influence of the type of fuel in the results.

A special consideration must be given to the here-presented option of burning a 100% excess of sulfur; while the amount of fossil fuel required would obviously be lower, the excess SO_2/SO_3 produced in the gas stream has to be scrubbed with CaO in order to meet environmental legislation and produce calcium sulfate that can certainly be used as an inter-grinding additive in the final cement product. Owing to the need for CaO production for the scrubber that has inherent CO_2 emissions, the stoichiometry of the process requires that at least 1 mol of CO_2 per mole of excess burnt sulfur is accounted for. In this case, an environmental burden from excess sulfur combustion must be added to the equation:

2013, has published the tonnes-km (tkm) of bauxite entering a number of industries in Europe and the US and via each transport mode: 19.4 tkm for rail, 1.4 tkm for road, and 2055 tkm for sea freight. Carbon emission factors for transport modes are taken from McKinnon (2007): 0.024 kg CO_2/tkm for rail, 0.09 kg CO_2/tkm and 0.03 kgCO_2/tkm. It is acknowledged that the emission factor for bauxite production calculated using this approximation is highly sensitive to the transport mode used; therefore, the sensitivity of the results to transport mode selection is analysed and discussed in the following sections.

2.5. Cost estimation

Due to the difficulty on estimating the required investment for the changes in the cement production facility when switching from PC to C\$A, only the change of operational expenses (OPEX) is evaluated. Results produced in this way may be read as relative cost variation of C\$A clinker manufacturing in a PC kiln with no major refurbishment to the installation. This methodology can be used to estimate the real cost variation when capital cost changes are known. As basis for the calculations, the OPEX model is the same as that from IEA, 2008 for PC production. The cost balance was modified to include natural gas as the only fuel used, and the amount of raw materials for Portland cement is changed to those reported by Chen et al. (2010) (same as the one used for the GHG balance). The cost of raw materials for C\$A manufacture and other assumptions are shown in Table 5. All costs are updated using the Producer Price Index by commodity for input to the industry from the U.S. government (Federal Reserve Economic Data, FRED, 2016)

{*emissions burden for excess sulfur combustion*}
$\approx$ {*emissions from calcination of calcite for scrubbing*}
$+$ {*emissions from the supply chain of excess sulphur*}
$-$ {*emissions avoided from natural gas combustion by burning sulphur*}
$-$ {*emissions avoided from using natural gypsum for inter* $-$ *grinding*}

3. Results

3.1. Carbon footprint of the analysed clinkers

All the assumptions and parameters used for the calculation, including the carbon intensities of raw materials, are shown in Table 4 below. The relative importance of these assumptions is tested in this work via a sensitivity analysis.

The carbon intensity for bauxite is calculated by considering the amount of bauxite that is supplied, on average, per transport mode (rail, road and sea). The International Aluminium Institute (IAI),

GHG emissions, calculated using the methodology described above, are shown in Fig. 2. All C\$A formulations proposed easily achieve a 25–35% reduction in emissions with small variations between gypsum and anhydrite sulfur sources, with slightly higher

Table 5
Assumptions for raw materials costing in C$A manufacturing.

Raw material/fuel	Cost	Unit	Assumptions and source
Limestone	3.20	EUR/tonne	Updated from International Energy Agency, 2008
Clay	1.6	EUR/tonne	Updated from International Energy Agency, 2008
Bauxite	28	EUR/tonne	U.S. Geological Survey, 2016
Sulfur	100	EUR/tonne	Jewell and Kimball, 2015
Natural Gas	0.01	EUR/MJ	Eurogas, 2013
Gypsum	10.50	EUR/tonne	Updated from International Energy Agency, 2008

N.B. All costs actualised to Eurogas, 2013

Fig. 2. Operational and supply chain emissions from C$A and PC clinker manufacturing. . The column labels have the following key: GY/AN/S correspond to Gypsum/Anhydrite/ Sulfur sources, numbers indicate ye'elimite fractions, and (exc) denotes 100% excess sulfur combustion.

emissions when using sulfur or excess sulfur in the raw feed. The main reduction of emissions in the production of C$A is linked to the lower requirement for calcined limestone. In the case of elemental sulfur, emissions are slightly higher due to the extra emissions burden from sulfur supply chain and those generated in the SO_2 capture process when feeding excess sulfur. In the case of using gypsum or anhydrite, the emissions from fuel consumption are like those from PC. It is observed that the reduction of GHG emissions from limestone calcination is not outweighed by the emissions brought about by the use of bauxite; thus, C$A clinker manufacture easily achieves significant GHG emissions savings

compared to PC.

When calcium sulfate is used as the sulfur source, higher ye'e-limite contents lead to lower emissions mainly due to the lower theoretical heat and the lower clinkering temperatures. This does not happen with sulfur combustion; the higher the ye'elimite content, the higher influence from the supply chain of sulfur, creating a trade-off which offsets the saving in emissions. Nevertheless, the variation of emissions from gypsum or anhydrite to sulfur combustion is relatively low and it is expected that the uncertainty in the raw data makes this variation unimportant.

A sensitivity analysis of the most important assumptions is produced: the Tornado chart in Fig. 3 shows the main results for the scenario of stoichiometric sulfur added to produce 50% ye'elimite clinker (644 kg CO_2e/tonne of clinker). The Tornado chart represents the variation of emissions when a certain parameter is varied by ±20% of its original value and the response from the emissions model is evaluated and plotted, producing a tornado-like shape when sorted. As shown in Fig. 3, the emissions from C$A clinker manufacturing are highly influenced by the combustion of fuel, while the emissions from the supply chain of materials have varying minor influence due to various reasons: limestone, as a matter of higher volume of use, and bauxite and sulfur, as a matter of relatively high impact. The rest of assumed parameters have negligible influence and have not been included in the chart.

3.2. Economics of production of 1 tonne of C$A clinker
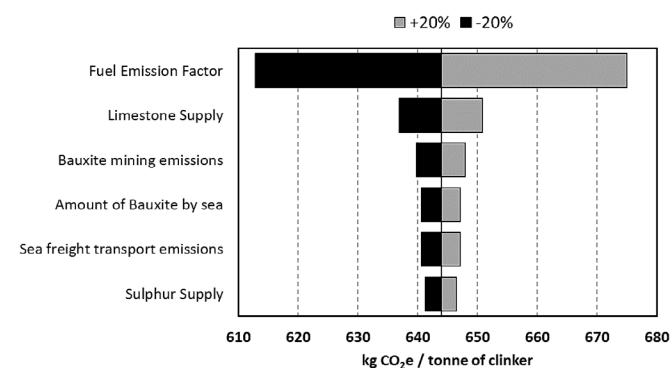
With regards to costs, the main results for the assumed

Fig. 3. Tornado chart showing the influence of the certain assumptions in the calculation of GHG emissions for C$A clinker manufacturing.
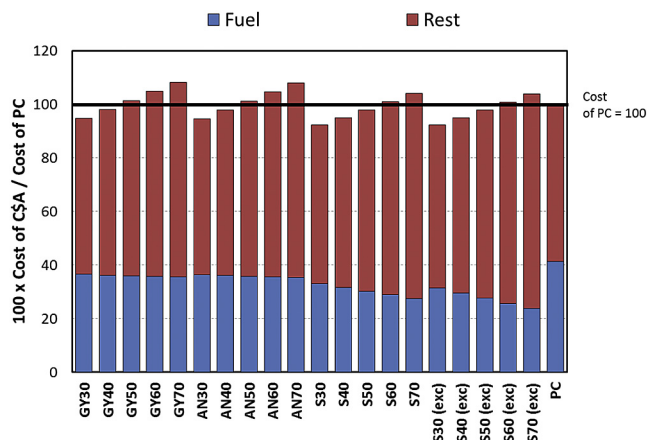
Fig. 4. Costs of C$A clinker manufacturing in relation to PC, low-cost bauxite.

Fig. 6. Cost per avoided tonne of CO_2 from C$A cement manufacturing in relation to PC manufacturing when the lower cost estimate of bauxite is used.

scenarios are shown in Fig. 4 relative to the cost of PC. Costs seem to be negatively influenced by compositions higher in ye'elimite as they require a higher amount of bauxite in the raw meal. The economic performance can be optimised if the amount of bauxite fed to the process is kept at a minimum value. The use of alternative raw materials with high Al_2O_3, such as high-alumina clays, is an option which has already been proven experimentally (Hanein et al., 2016b); however, costs, availability, and geographic distribution would require a deeper analysis. Fuel costs are reduced for all C$A options and are further reduced in cases of sulfur combustion.

The similarity of costs between C$A and PC is a significant result of these calculations; however, there are undeniable uncertainties regarding the sources of data. For instance, the cost for bauxite was taken from the USGS, as it accounts only for the U.S. imports while the average carbon dioxide emissions were calculated using the published data by International Energy Agency, 2008, from a survey made to several bauxite suppliers. The assumption of higher costs for bauxite, EUR 144 per tonne, using the average transport distances per mode reported by International Energy Agency, 2008, has a significant negative impact on the economy of high-ye'elimite C$A as demonstrated in Fig. 5. While all C$A formulations appear to reduce the emissions from PC independently of the content of ye'elimite, the cost of bauxite has a key influence on the economic optimum of ye'elimite content. A high ye'elimite clinker can cost
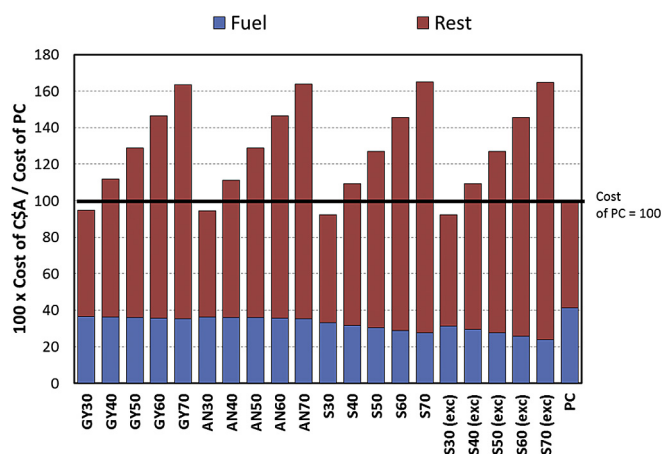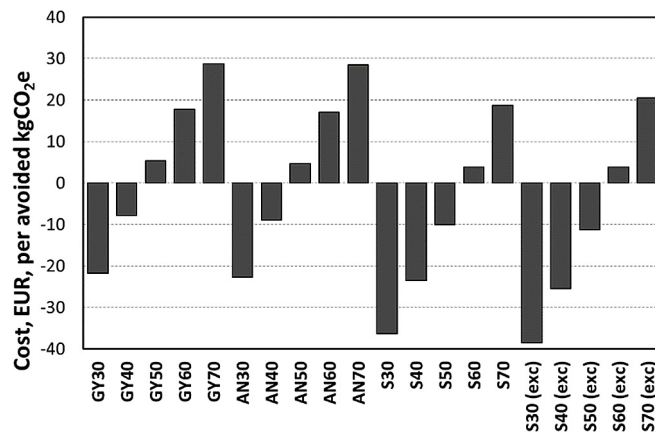
60% more than PC in the worst-case scenario of bauxite shipping costs.

In all cases, the C$A costs are heavily dependent on the content of ye'elimite which is identified as the main element of C$A price uncertainty. In fact, the most economical formulations are those showing a minimum content of ye'elimite, which is in opposition to the associated carbon footprint. To evaluate better this transition from PC to C$A in terms of carbon intensity of the industry, the cost of reducing a tonne of CO_2 by switching from PC to C$A has been calculated as the variation of costs divided by the variation of emissions (see Fig. 6) from PC for each C$A clinker (the lower cost estimate of bauxite is used).

As observed in Fig. 6, higher ye'elimite contents yield higher CO_2 avoidance costs. The negative value of this cost indicates savings brought about by using C$A cement as an alternative to PC. The use of sulfur produces a lower cost of avoidance than any option using gypsum, as is expected from the lower theoretical heat, and the amount of compensated heat from natural gas produces more savings than the higher associated emissions of sulfur in comparison to gypsum or anhydrite.

4. Discussion

This systematic study has shown that C$A clinker formulations based on ye'elimite, can have a lower carbon footprint than PC while remaining cost competitive under certain (but not unusual) economic conditions. As C$A requires a higher content of sulfur fed in the raw meal this can be supplied through elemental sulfur, which can act also as fuel or be provided through calcium sulfate which can be sourced from natural or recycled gypsum. Given the emissions allocated to elemental sulfur, no significant environmental difference between these options is observed; however, high ye'elimite content cements require higher amounts of bauxite or high alumina clays in the raw feed, which negatively affects the economics of the process. These facts have previously been predicted by many experts in the field (Gartner and Hirao, 2015) and this work provides a quantitative verification of those qualitative assumptions. All the results presented in this work are only valid under the many different assumptions required to carry out the calculations and the various circumstances around the life cycle of the assessed cements.

In general, the production of C$A clinker requires less energy than ordinary PC. The lower theoretical heat requirements for C$A production are reflected in the calculations shown above; however, no changes are assumed for the thermal efficiency of the kiln,
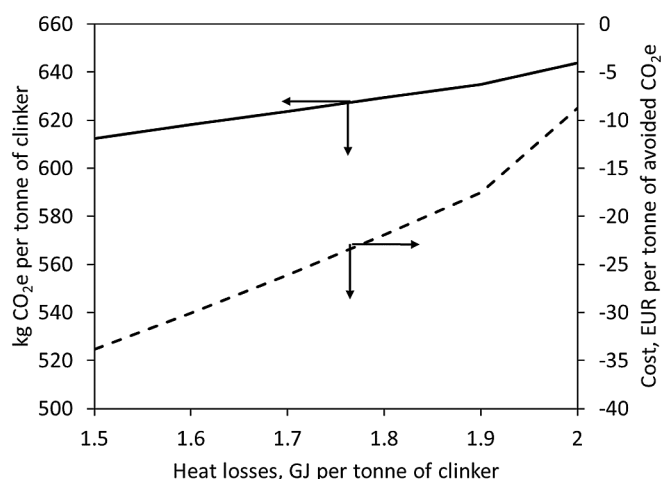

Fig. 5. Costs of C$A clinker manufacturing in relation to PC, average cost bauxite.

Fig. 7. Influence of kiln heat losses on the carbon footprint (solid) and cost per tonne of avoided CO_2e (dashed) for C$A clinker with 50% ye'elimite produced by burning stoichiometric sulfur.

which is assumed the same for C$A and PC. As explained, heat losses are assumed to be around 2 GJ per tonne of clinker for both, but it is suspected to be lower in efficient modern kilns operating at lower burning temperature. If the gas mixture exhaust of PC clinker production, as described by the European Commissions' best available techniques reference document (Eurogas, 2013) for the cement industry is used (21%CO_2, 12.3% O_2, 62%N_2, H_2O 4%) and the temperature is reduced from 1450 °C to 1250 °C, a saving in sensible heat of 1 GJ per tonne of clinker would be achievable. However, main heat losses due to radiation and also those at the lower temperature end of the kiln are difficult to estimate.

To illuminate the effects of a better kiln efficiency, the influence of the heat losses on the carbon footprint and cost of C$A clinker with 50% ye'elimite produced with sulfur is shown in Fig. 7. It is observed that the variation in emissions is not as significant as the influence on costs. Carbon dioxide emissions from C$A production vary from 610 to 644 kg CO_2e per tonne of clinker (a 5% maximum variation), while the cost of CO_2 avoidance increases significantly, i.e. more than 70%, as the efficiency decreases. In the example of Fig. 7, negative costs indicate savings in comparison to PC that are improved when the efficiency of the kiln is higher. This means that higher operational expenses from more expensive raw materials might be compensated by the improved thermal efficiency in a modern C$A clinker production facility.

Another interesting aspect is the source of sulfur. Elemental sulfur is assumed to be sourced from the desulfurisation of fossil fuels. Although it may be thought of as a waste, it is defined as a product due to its usually high quality, wide market, and relative high demand; thus, the associated emissions and a price are assumed in this work. In the case of calcium sulfate, it can be sourced from a natural origin, but it can also be sourced from wasted plasterboard and, especially, as a by-product from the desulfurisation of flue gases in power plants. It shall be considered a waste: the producer wants to dispose of it, and its demand as secondary material does not cover the whole production of this so-called "waste". The associated supply chain emissions of the calcium sulfate "waste" are null (except for the transportation to the cement production site). Therefore, calcium sulfate wastes can be preferred against elemental sulfur according to the sensitivity analysis performed in this work; a 50% ye'elimite C$A clinker tonne has a carbon footprint of 595 kg CO_2e if produced from natural gypsum, 644 kg CO_2e if elemental sulfur is used, and would have only 588 kg CO_2e if recycled calcium sulfate is used.

On top of the options assessed, the use of sulfur-bearing fossil fuels, e.g. non-desulfurized natural gas, pet coke, etc., may constitute a preferable option against other sources, since (1) the absorption of sulfur is likely to be similar at kiln operating conditions, (2) the fuel source is cheaper and (3) the theoretical heat required for C$A clinker manufacturing would be reduced, since the oxidation state of sulfur is −2 (if H_2S is assumed), allowing increased available heat from sulfur oxidation. This option has not been included in this assessment as no experimental work in this respect is available; however, the prospective use of H_2S-bearing natural gas would allow an important reduction of energy consumption in the kiln (Hanein et al., 2016a). Also, although some "sour" fuels such as pet-coke cannot be used as the sole sulfur source for C$A clinker manufacture (due to their low sulfur weight content (<6%)), the use of such fuels will provide an economic benefit as high sulfur-containing fuels are generally cheaper than low sulfur-containing fuels and the additionally required sulfur can be supplemented via any of the other means already discussed.

The results presented here demonstrate that the source of alumina is critical to the economic performance of the process. Al_2O_3 can be supplied from high alumina clays and the economics of using clays are more favourable than situations where the raw feed includes sources of bauxite; however, the analysis performed only considers marginal changes, i.e. the production of C$A cement does not impact the economic system. It is envisaged that mass production of C$A cements would have an enormous impact on the economics of bauxite sourcing. Probably, the higher demand on a resource such as bauxite, only available in specific geographical locations, would generate a serious limitation on the commercialisation of low-carbon C$A cements.

Due to the substantial reduction in CO_2 emissions offered by C$A clinker compared to PC clinker, carbon taxation is another aspect which could significantly sway the course of commercial cement manufacture in favour of C$A in the near future. A number of countries have already implemented CO_2 taxation (notably not yet the USA and China) and the cost of emitting CO_2 is increasing. Further CO_2 taxation increases are expected as it is foreseen to be one of the major drivers of the Paris Agreement (United Nations, 2015) within the United Nations Framework Convention on Climate Change that went into action in November 2016 and will start tackling GHG mitigation in 2020.

5. Conclusions

The production of C$A clinkers, as an alternative to PC, demonstrates a reduced carbon footprint, mainly due to the lower amount of limestone required in the raw feed and the improved energetics. This reduction is independent of the source of sulfate although sulfur combustion in the kiln carries slightly higher emissions and lower production cost than calcium sulfate. The difference between sulfur sources is relatively small and, therefore, within the uncertainty of the study.

Emissions trade-offs were identified, especially from the operation of the kiln and the supply of raw materials (e.g. aluminium oxide sourcing). Overall, net emissions are reduced 25–35% subject to certain limitations on the geographical scope, the functional unit, and the assumptions on the fuel.

The introduction of bauxite as raw material for cement has a significant influence on costs, but this study demonstrates a significant potential for optimisation, e.g. the raw materials, the ye'elimite content of the clinker, the energy performance of the kiln, and the probable suitability of sulfur-bearing fossil fuels. If relatively cheap sources of aluminium oxide can be found and no deep modifications of the kiln technology are required, current production costs are competitive and CO_2 avoidance costs are

negative for the cement industry, suggesting that low CO_2 cement clinker production is also economically preferable.

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