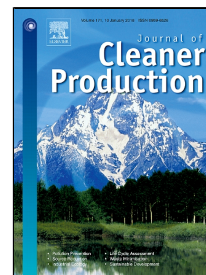


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**Carbon footprint of calcium sulfoaluminate clinker production**

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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.

*Keywords*

Cement, clinker, calcium sulfoaluminate, life cycle assessment, greenhouse gases, carbon dioxide, sulfur, calcium sulfate, bauxite

27 *Abbreviations*

28	CO <sub>2</sub> e	Equivalent CO <sub>2</sub> emissions
29	C\$A	Calcium SulfoAluminate
30	ELCD	European Life Cycle Database
31	GHG	Greenhouse gases
32	IAI	International Aluminium Institute
33	OPEX	Operational expenses
34	PC	Portland cement
35	STP	Standard temperature and pressure
36	tkm	Tonne-kilometre
37	USGS	United States Geological Survey
38	XRF	X-ray fluorescence

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39 **1. Introduction**

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

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

56 Market uptake of novel formulations of cement binders to be used in general construction applications is hindered  
57 by the lack of standardisation, which in turn delays the subsequent use of these new binders by the construction  
58 industry. However, “new” binders can bring mid-term emissions reductions without any major disruptive changes or  
59 the requirement of large capital investment in plant redesign (WBCSD, 2009a). Amongst the alternative binders  
60 proposed so far, calcium sulfoaluminate (C\$A) cements containing significant fractions of ye’elite are particularly  
61 promising (Juenger et al., 2011). C\$A cements require less calcium per tonne than PC thus the amount of CO<sub>2</sub>  
62 released through the calcination of calcium carbonates in limestone, chalk, and marble is reduced (Gartner, 2004;  
63 Quillin, 2009). The manufacture of C\$A still utilizes a kiln process; however, the process efficiency is improved  
64 when compared to PC production due to the more favourable theoretical heat requirements of C\$A compositions  
65 (Hanein et al., 2016a). Gartner, 2004, identified C\$A cements as low carbon cements suited for specialized  
66 applications with high early strength requirements; also, as an additive to other binders to control shrinkage or  
67 expansion; however, optimised compositions of C\$A can also provide a similar performance to PC with a potentially  
68 significant reduction in GHG emissions if used as mass for mass substitute. The high fraction of bauxite typically  
69 required in the raw meal makes C\$A cements relatively more expensive than Portland cement (Juenger et al., 2011);  
70 however, it has been proven that an economically-optimised composition can be achieved with high alumina clays  
71 (Hanein et al., 2016b) or even Al<sub>2</sub>O<sub>3</sub>-rich wastes (Gartner and Hirao, 2015).

72 Due to the enormous scale of cement production, careful consideration must be given to the abundance of the raw  
73 materials for any new formulation. The raw materials for C\$A cement manufacture differ from those used for PC.  
74 The C\$A clinkering process requires a source of sulfur which can be supplied as calcium sulfate, i.e. gypsum or  
75 anhydrite, which are naturally sourced (mined) or recovered from waste (e.g. from flue gas desulfurisation) or raw

76 sulfur, which can be burnt as a fuel (Hanein et al., 2016b). The annual world production of elemental sulfur is 72.4  
77 Mt/yr (Jewell and Kimball, 2015) and is rising due to an increasing reliance on sulfur-containing resources and  
78 environmental restrictions, most notably the low sulfur levels required in refined products such as diesel. Apart from  
79 being readily available to locations near oil and gas refineries, elemental sulfur can also be found and mined near hot  
80 springs and volcanic regions in many parts of the world and is well distributed geographically. Current annual  
81 elemental sulfur production is sufficient to produce  $\approx 3500$  Mt/yr of a C\$A clinker of 40% ye'elinite which is almost  
82 equivalent to the current world demand for cement; thus, the availability of sulfur would not be concern if C\$A  
83 cements were adopted in mass. Depending on the final formulation, sources of bauxite may also be required due to  
84 the higher need for aluminium oxide in calcium sulfoaluminate cements which cannot normally be provided from  
85 clays and/or shales only. This appears to be the key limitation in the commercial production of C\$A clinkers (Gartner  
86 and Hirao, 2015); however, other limitations may also appear due to the higher demand of gypsum for C\$A clinkers  
87 manufacturing.

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

## 97 **2. System definition, data sources, and assumptions**

### 98 *2.1. Goal, scope, and functional unit*

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

109 It is common practice that when comparing products the basis of the calculation, i.e. the functional unit in LCA  
110 terminology, corresponds to the amount or value of a product that provides the same service or function. This implies  
111 that the same functionality of each analysed clinker should be compared rather than a fixed quantity; however, a final  
112 use (e.g. civil construction) or final product (e.g. a concrete block) is difficult to define for two types of cements due

113 to the diverse applications, the different mineralogy, and the performance of the final formulation of the cement in  
114 terms of strength and durability. The functionality of C\$A cements, regarding these issues, is not yet well developed  
115 and standardisation of C\$A products is yet to be achieved in the western world. The problem with the characterisation  
116 of a functional unit for different cement formulations can be well understood through the clinker factor, which is the  
117 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  
118 cementitious wastes or SCMs such as pulverised fly ash, silica fume, or ground granulated blast-furnace slag, are  
119 added to the final product; the use of SCMs is one of the key GHG reduction potentials of PC manufacture (Boesch  
120 and Hellweg, 2010). The same is observed with cement mineralogy; currently, lower content ye'elinite and higher  
121 content reactive belite clinkers called BYF (belite-ye'elinite-ferrite) have been developed to reduce the use of bauxite  
122 in the raw meal and improve the performance of the cement (Gartner and Sui, 2017).

123 Unfortunately, comparable cement formulations of C\$A and PC are rather limited by the type of additions, their  
124 mineralogy, and their environmental performance which depends on the inherent properties of the final products. For  
125 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  
126 with almost no addition to the clinker or with rather low additions of other materials as gypsum (Beltagui et al, 2017).  
127 It is fair to say that C\$A products are still not well understood and the optimisation towards competitive commercial  
128 C\$A products is still limited. For instance, C\$A formulations including fly ash are found to be reliable (Garcia-Mate  
129 et al., 2013) but large-scale application is yet to be attempted. Due to the aforementioned reasons, and to facilitate  
130 the benchmarking of production processes rather than products, this study compares emissions and costs per tonne  
131 of *clinker*. The results of this work may be considered for the calculation of the environmental impact of cement-  
132 based products; but, any use of the results must consider the implications of the assumptions made.

## 133 2.2. Methodology

134 Carbon dioxide is the main culprit of the so-called greenhouse effect. Prior to the industrial revolution; atmospheric  
135 CO<sub>2</sub> concentrations were fairly stable at 280 ppm but today are around 400 ppm. Other anthropogenic emissions also  
136 have a considerable environmental effect, e.g. methane, nitrous oxide, and fluorinated gases; the effect of these other  
137 gases is often accounted for as an equivalent mass of CO<sub>2</sub> which produces the same effect, i.e. equivalent CO<sub>2</sub> or  
138 CO<sub>2</sub>e. As each gas is active over different timescales, the CO<sub>2</sub>e calculated in this document uses effects within 100  
139 years as a basis in line with the approach of the Intergovernmental Panel on Climate Change (Simmons, 2007). The  
140 use of mass of CO<sub>2</sub>e as a measure of the greenhouse effect is also quite well known as the Global Warming Potential,  
141 GWP, in the field of LCA. The amount of equivalent emissions per tonne is known as the emission factor, carbon  
142 intensity or carbon footprint.

143 Using this methodology, the emissions from the supply chain of raw materials consider the whole amount of  
144 equivalent CO<sub>2</sub>, including e.g. 21 kg CO<sub>2</sub>e per kg of methane, or 298 kgCO<sub>2</sub>e per kg of N<sub>2</sub>O. However, the operational  
145 emissions balance of clinker production only considers real CO<sub>2</sub> emissions from the internal processes such as  
146 combustion and calcination.

147 The GWP is calculated using an *attributorial* approach, i.e., environmental pressures are associated to every mass  
148 and energy input or output of the process. This methodology assumes that there are no relevant changes in the impacts  
149 arising from the supply chain due to the production of a new product. This is opposed to *consequential* analyses,  
150 where the influence of the new process, product, or service is calculated according to certain economic equilibrium

151 rules. For instance, manufacturing C\$A cement at global scale would certainly affect the economy of bauxite, high  
 152 alumina clays, and/or alumina-bearing wastes, and of course impact on their logistics and thus the environment. For  
 153 simplicity, this is not considered in this work and, to validate the applicability of the results of this study, further  
 154 research will be required if C\$A manufacture is adopted at scale.

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

### 158 2.3. *Product system*

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

163 Chemically, the primary difference between C\$A and PC clinkers is their mineralogy; C\$A contains ye'elite,  
 164 ( $C_4A_3\$$ ), rather than alite ( $C_3S$ ) as a major constituent (Juenger et al., 2011). Both clinkers contain belite ( $C_2S$ ) and  
 165 ferrite ( $C_2(A,F)$ ); N.B. for simplicity, all cement clinker phases are expressed using the oxide notation outlined in  
 166 Table 1, using \$ to refer to  $SO_3$ . The raw feed used in the conventional manufacture of cement contains oxides of  
 167 calcium, silicon, aluminium and iron, plus other minor components that are usually supplied from readily-available  
 168 low-cost sources; calcium oxide is the major/key component. Limestone, composed primarily of  $CaCO_3$ , is generally  
 169 the main source of calcium for all cement manufacturers (chalk and marble may also be used) and has a significant  
 170 effect on the GHG emissions as it needs to be calcined into lime ( $CaO$ ) and  $CO_2$  through high temperature treatment.  
 171 The remaining ingredients required for the raw mix are usually supplied from siliceous clays, shales, and/or fly ash.  
 172 The substantially lower lime factor in the mineralogy of C\$A reduces the amount of limestone needed when  
 173 compared to PC, but brings about an increase in the amount of alumina and sulfur oxides required in the raw meal.  
 174 Alumina-rich clays have already proven to be effective (Hanein et al., 2016b) as substitute of the more conventional  
 175 bauxite. Industrial by-products such as slag have also been successfully utilised as an alumina source (Whittaker et  
 176 al, 2014); however, alumina sources are scattered in their global distribution and carry higher burdens of  $CO_2e$   
 177 emissions due to higher needs of transport and distribution (IAI, 2013).

178 **Table 1. Cements oxides notation used in this work**

Oxide	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>
Notation	C	S	A	F	\$

179

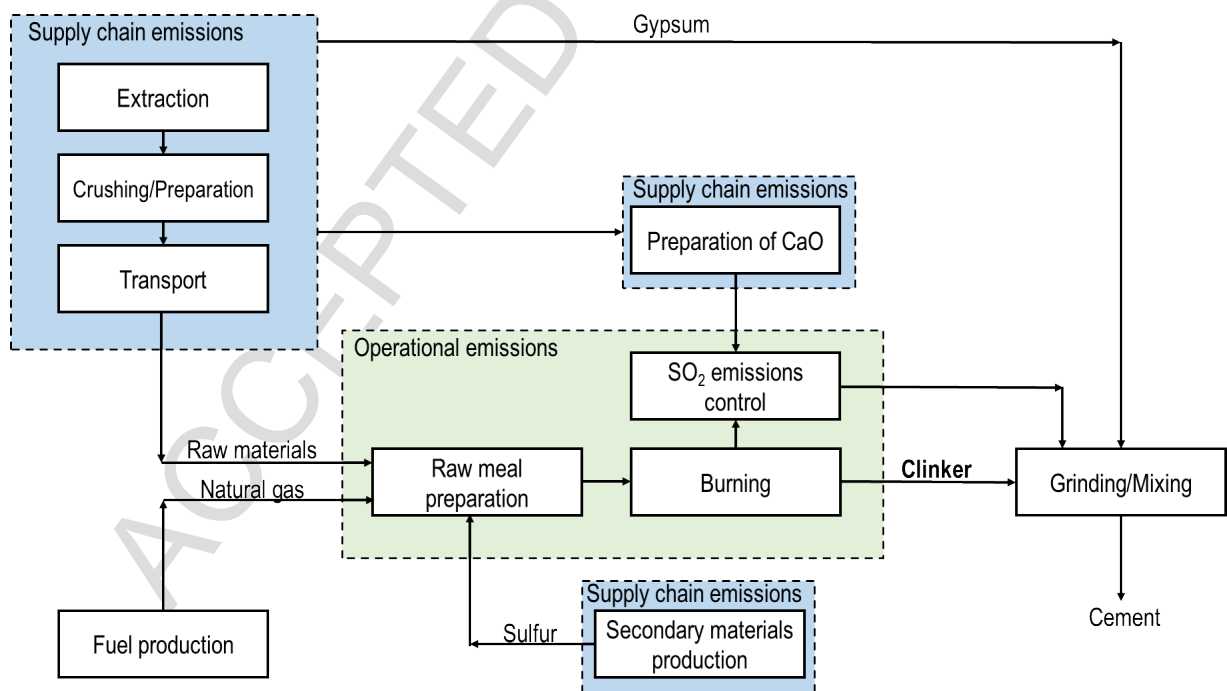
180 To produce the clinkers for both types of cement (PC and C\$A), the raw materials are sintered using fuels such as  
 181 pet coke, coal, and waste-derived fuels that provide the necessary heat and temperature required to produce clinker  
 182 with a specific phase assemblage. The use of coal or pet coke is associated with high  $CO_2$  emissions while waste-  
 183 derived fuels, although allowing for a better economic performance of the process, do not produce a statistically  
 184 significant reduction in emissions (Galvez-Martos and Schoenberger, 2014). Elemental sulfur is a by-product which  
 185 arises from the Claus process employed during the desulfurization of sulfur-rich (sour) oil and gas; it is therefore  
 186 readily available. It has already been demonstrated that the products of sulfur combustion, sulfur dioxide and oxygen,

187 are readily transferred from the gas phase to the solids to form clinker phases such as ye'elimite (Strigac and Majling,  
188 1997). Of course, the combustion of sulfur does not produce CO<sub>2</sub>; however, the following must be considered:

- 189
- 190 • Although sulfur is a by-product, it has a relatively healthy demand, e.g. to produce sulfuric acid, and it also  
191 has a non-negligible price around EUR 90-100 per tonne (Jewel and Kimball, 2015). Therefore, it is not  
192 considered a waste and any LCA where sulfur is an input should consider emissions from its production  
193 process. According to the European Commission ELCD database, emissions from sulfur production are 489  
194 kg CO<sub>2</sub>e per tonne; this value is used in this work.
  - 195 • The combustion of excess sulfur (to that incorporated in the clinker) is required due to chemical equilibrium  
196 constraints and produces excess SO<sub>x</sub> gas at the exhaust of the kiln. Due to the negative environmental impact  
197 of this gas, these emissions must be abated by reaction with calcium oxide and oxygen to produce solid  
198 calcium sulfate, most probably via the more efficient wet process. This simple process has a non-negligible  
199 carbon footprint as CO<sub>2</sub> is produced in the calcination of limestone to produce the CaO that is used as the  
200 absorbent. At the same time, the produced calcium sulfate can substitute the natural gypsum used as an inter-  
201 grinding additive in the manufacture of cement from clinker. These emission trade-offs are considered in this  
study.

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

206



207

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

209 2.4. Assumptions



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

$$\begin{aligned}
 & \{emissions\ from\ C\$A\ clinker\ production\} \\
 & \approx \{emissions\ from\ CaCO_3\ calcination\} + \{emissions\ from\ fuel\ combustion\} + \\
 & \{emissions\ from\ the\ supply\ chain\ of\ materials\} \quad Eq. (1)
 \end{aligned}$$

213 Equation 1 is a simplification of the full emissions balance as many secondary processes also have associated  
 214 emissions; however, most of the CO<sub>2</sub>e emissions from cement production can be accurately predicted from a set of  
 215 six parameters, as defined by Ammenberg et al., 2011 and corroborated by Galvez-Martos and Schoenberger, 2014:  
 216 (1) clinker factor, (2) CO<sub>2</sub> emissions from calcination, (3) final energy consumption (as fuel) (4) share of cleaner  
 217 fuels (e.g. from biogenic sources), (5) specific electrical energy consumption, and (6) share of renewable electricity.  
 218 The impact from the post-production phase, e.g. electricity consumption in the clinker grinding process, is excluded  
 219 as it is assumed to be similar to that of PC clinkers; however, studies have shown that C\$A clinker is easier to grind  
 220 than PC clinker thus it is likely that this assumption favours PC (Schneider, 2015).

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

226 To design the various raw mixtures, the compositions of the clay, limestone, gypsum, and bauxite used in this work  
 227 are obtained from the raw materials used in the previous pilot-scale trials (Hanein et al., 2016b and 2017) as X-ray  
 228 Fluorescence (XRF) analysis of their composition is available and they are representative of the raw products  
 229 commercially available in large volumes: limestone (Samin, France), clay (Zhengzhou Haixu abrasives, China),  
 230 bauxite (Zhengzhou Haixu abrasives, China), and gypsum (Saint-Gobain, United Kingdom). The oxide composition  
 231 of the limestone and gypsum were provided by the respective suppliers. As economical cement production must use  
 232 local mineral sources which can have significant variation in composition depending on the location of the plant, the  
 233 results presented here do not immediately generalise to production everywhere but provide an illustrative example.  
 234 Anhydrite is assumed here to be pure CaSO<sub>4</sub>. The major oxide compositions of the raw materials are shown in Table  
 235 2.

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

	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	SO <sub>3</sub>
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

237 The composition of the theoretical raw meal is calculated for C\$A clinker outputs containing between 30 and 70%  
 238 ye'elinite, 10% ferrite (C<sub>4</sub>AF), and the remaining as belite. A constrained optimisation is performed to minimise the  
 239 amount of bauxite required (to allow favourable economics) while meeting the minimum ye'elinite content  
 240 requirements and ensuring no free lime or anhydrite is present in the system (which are undesirable products). The  
 241 ferrite content is unconstrained and varies between 2-10%. The assumptions made for the raw material calculations  
 242 include the following: (1) all alkali react to form alkali sulfates, (2) all TiO<sub>2</sub> react to form CaTiO<sub>3</sub>, (3) all silica react

243 to form belite, (4) all iron reacts to form ferrite ( $C_4AF$ ), (5)  $MgO$  is unreactive, and (6) no sulfur is lost during pyro-  
 244 processing. For each formulation, the calculated compositions of raw materials are shown in Table 3. It should be  
 245 noted that the actual C\$A clinker output does not only depend on the raw mix but also on the conditions in the  
 246 clinkering zone including temperature and  $SO_2$  and  $O_2$  partial pressure (Hanein et al. 2017). For simplicity, it is  
 247 assumed that the kiln is operated such that the conditions within the kiln are appropriate for C\$A manufacture without  
 248 considering the operational challenges this implies in maintaining an adequate  $SO_2$  atmosphere.

249  
 250

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

Source of sulfur	Target formulation $C_4A_3S$ (%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

251 For the theoretical heat calculations, silica is assumed to be introduced as kaolinite ( $Al_2Si_2O_5(OH)_4$ ) and pyrophyllite  
 252 ( $Al_2Si_4O_{10}(OH)_2$ ). The remaining alumina not furnished as kaolin or pyrophyllite is introduced as gibbsite ( $Al(OH)_3$ ),  
 253 while all iron is assumed to be introduced as goethite ( $FeO(OH)$ ). All calcium is assumed to be introduced as calcium  
 254 carbonate ( $CaCO_3$ ) except for any that is present in gypsum and/or anhydrite when they are used. Thus, the theoretical  
 255 heat demand of the kiln process is calculated from the change in the enthalpy content from the raw materials to the  
 256 final product. The reference heat of formation at STP of ye'elimite is taken to be  $-8406.493$  kJ/mol (Costa et al.,  
 257 1972). Data for goethite ( $FeO(OH)$ ) and gypsum ( $CaSO_4 \cdot 2H_2O$ ) are taken from Wagman et al, 1982, and the data for  
 258 the remaining phases are taken from a thermodynamic dataset recently compiled by Hanein et al., 2015. The total  
 259 heat demand of the kiln process is thus the sum of the theoretical heat plus an assumed fixed heat loss taken from the  
 260 PC manufacturing kiln processes which is 2GJ per tonne of clinker (calculated from WBCSD, 2009b). A deeper  
 261 analysis of the thermal efficiency of the kiln is required to take into account heat loss variations (compared to PC)  
 262 brought about by the lower temperature required for C\$A clinker manufacture, the associated change of gas flow,  
 263 changes in chemical composition, and the different thermal behaviour at the low temperature end of the gas exhaust.  
 264 Due to the lack of information on the performance of C\$A kilns, the average thermal loss from PC clinker  
 265 manufacturing, 2GJ, has been assumed for C\$A clinkers.

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

275 Natural gas is used here as the fuel source; however, other fuels such as coal or solid residue fuel are also frequently  
 276 combusted in cement making. The lack of experience of alternative fuels with C\$A and the harmonisation required  
 277 on the assessment to evaluate the influence of the introduction of sulfur are the two main reasons behind this  
 278 approximation. Both issues needed to be solved, from a mass and energy balance perspective, by assuming the same  
 279 fuel for both C\$A and PC clinkers, so that the influence of other parameters of the product system could be isolated.  
 280 In fact, it is expected that waste-derived fuel or pet coke will be richer in sulfur, which would in turn favour the  
 281 formation of C\$A cements. As C\$A also has a lower heat demand than PC, the use of natural gas leads to a  
 282 conservative estimate of the reduction in fuel derived CO<sub>2</sub> emissions when compared to PC. Another reason to  
 283 exclude “usual” fuel mixes is the uncertainty of the GHG balance (Galvez-Martos and Schoenberger, 2014) when  
 284 considering wastes and solid residue fuels. These fuels tend to produce economic savings but the impact on emissions,  
 285 although often claimed to be positive, has little statistical significance. By simplifying the fuel to natural gas, a  
 286 common emissions basis can also consider the fuel economy of the kiln and remove the influence of the type of fuel  
 287 in the results.

288 A special consideration must be given to the here-presented option of burning a 100% excess of sulfur; while the  
 289 amount of fossil fuel required would obviously be lower, the excess SO<sub>2</sub>/SO<sub>3</sub> produced in the gas stream has to be  
 290 scrubbed with CaO in order to meet environmental legislation and produce calcium sulfate that can certainly be used  
 291 as an inter-grinding additive in the final cement product. Owing to the need for CaO production for the scrubber that  
 292 has inherent CO<sub>2</sub> emissions, the stoichiometry of the process requires that at least 1 mole of CO<sub>2</sub> per mole of excess  
 293 burnt sulfur is accounted for. In this case, an environmental burden from excess sulfur combustion must be added to  
 294 the equation:

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

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

299 Table 4. Assumptions, emissions factors and carbon intensities for the calculation of the GHG balance of C\$A  
 300 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 <sup>3</sup>	Eurogas, 2013
Heat from sulfur combustion	9.278	MJ/kg	Eckamn, Rossini, 1929
Emission factor, natural gas combustion	0.056	kg CO <sub>2</sub> e /MJ	U.S. EIA, 2016
Emission factor, supply of limestone	38	kg CO <sub>2</sub> e/tonne	ELCD, 2006
Emission factor, supply of sulfur	489		ELCD, 2003
Emission factor, supply of gypsum/anhydrite	50		Fisher, 2008.
Emission factor bauxite, mining (a)	11		Aluminium Association, 2013
Emission factor bauxite, transport (b)	62		IAI, 2013; McKinnon, 2007
Emission factor, supply of bauxite (a) + (b)	140		Calculated
Emission factor, supply of clay,	3.7		Koroneos and Dompros, 2007.

301 The carbon intensity for bauxite is calculated by considering the amount of bauxite that is supplied, on average, per  
 302 transport mode (rail, road and sea). The International Aluminium Institute (IAI), 2013, has published the tonnes-km  
 303 (tkm) of bauxite entering a number of industries in Europe and the US and via each transport mode: 19.4 tkm for rail,  
 304 1.4 tkm for road, and 2055 tkm for sea freight. Carbon emission factors for transport modes are taken from McKinnon,  
 305 2007: 0.024 kg CO<sub>2</sub>/tkm for rail, 0.09 kg CO<sub>2</sub>/tkm and 0.03 kgCO<sub>2</sub>/tkm. It is acknowledged that the emission factor  
 306 for bauxite production calculated using this approximation is highly sensitive to the transport mode used; therefore,  
 307 the sensitivity of the results to transport mode selection is analysed and discussed in the following sections.

#### 308 2.5. Cost estimation

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

318

Table 5. Assumptions for raw materials costing in CSA manufacturing

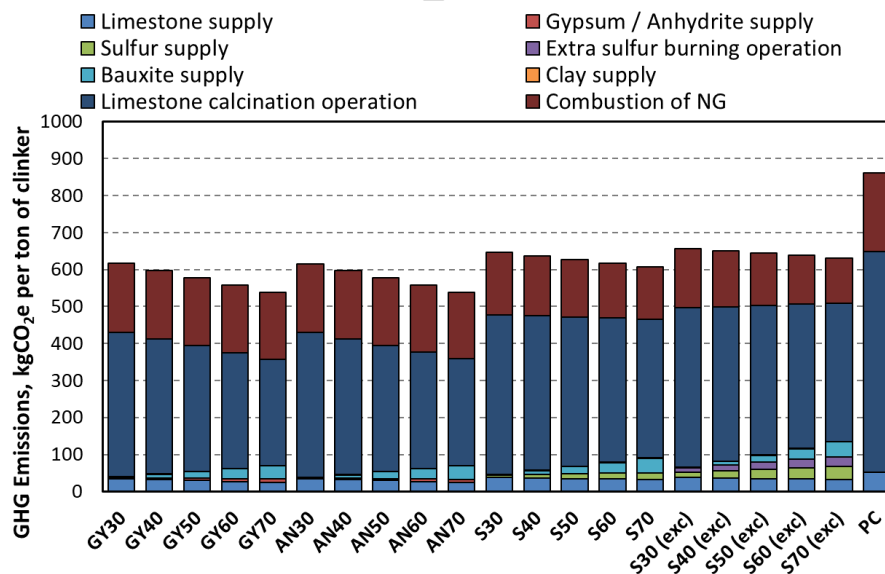
Raw material/ fuel	Cost	Unit	Assumptions and source
Limestone	3.20	EUR/tonne	Updated from IEA, 2008
Clay	1.6	EUR/tonne	Updated from IEA, 2008
Bauxite	28	EUR/tonne	USGS, 2016
Sulfur	100	EUR/tonne	Jewel and Kimball, 2015
Natural Gas	0.01	EUR/MJ	Eurogas,2013
Gypsum	10.50	EUR/tonne	Updated from IEA, 2008

N.B. All costs actualised to EUR 2016

### 3. Results

#### 3.1. Carbon footprint of the analysed clinkers

GHG emissions, calculated using the methodology described above, are shown in Figure 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 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<sub>2</sub> 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.



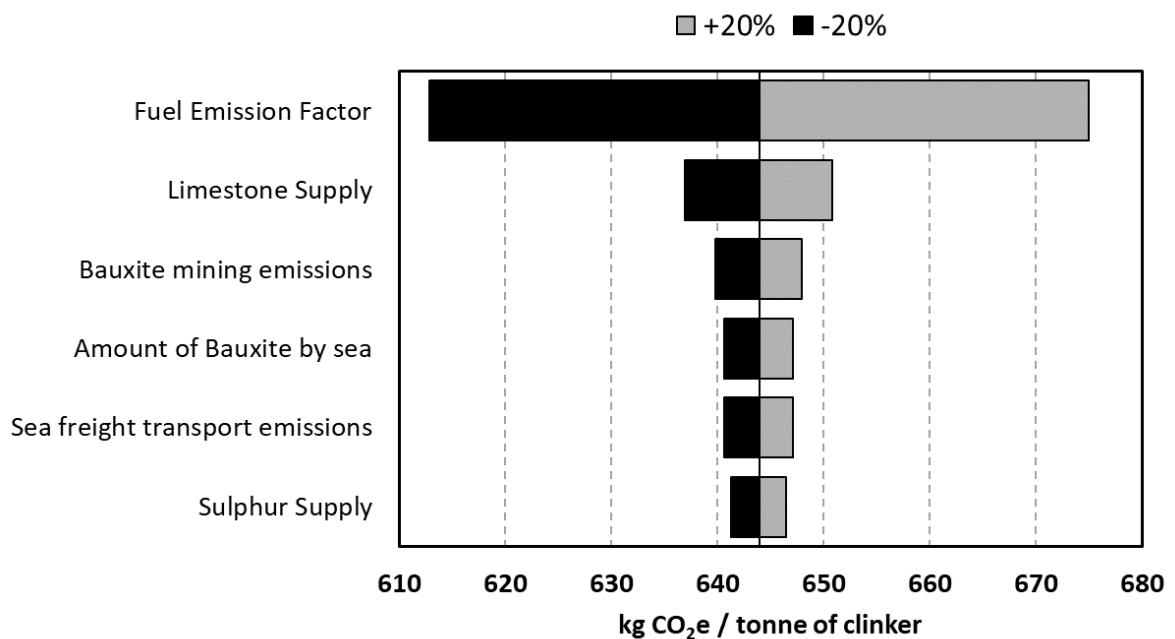
331

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

335 When calcium sulphate is used as the sulfur source, higher ye'elimate contents lead to lower emissions mainly due to  
 336 the lower theoretical heat and the lower clinkering temperatures. This does not happen with sulfur combustion; the  
 337 higher the ye'elimate content, the higher influence from the supply chain of sulfur, creating a trade-off which offsets

338 the saving in emissions. Nevertheless, the variation of emissions from gypsum or anhydrite to sulfur combustion is  
 339 relatively low and it is expected that the uncertainty in the raw data makes this variation unimportant.

340 A sensitivity analysis of the most important assumptions is produced: the Tornado chart in Figure 3 shows the main  
 341 results for the scenario of stoichiometric sulfur added to produce 50% ye'elinite clinker (644 kg CO<sub>2</sub>e/tonne of  
 342 clinker). The Tornado chart represents the variation of emissions when a certain parameter is varied by ±20% of its  
 343 original value and the response from the emissions model is evaluated and plotted, producing a tornado-like shape  
 344 when sorted. As shown in Figure 3, the emissions from C\$A clinker manufacturing are highly influenced by the  
 345 combustion of fuel, while the emissions from the supply chain of materials have varying minor influence due to  
 346 various reasons: limestone, as a matter of higher volume of use, and bauxite and sulfur, as a matter of relatively high  
 347 impact. The rest of assumed parameters have negligible influence and have not been included in the chart.

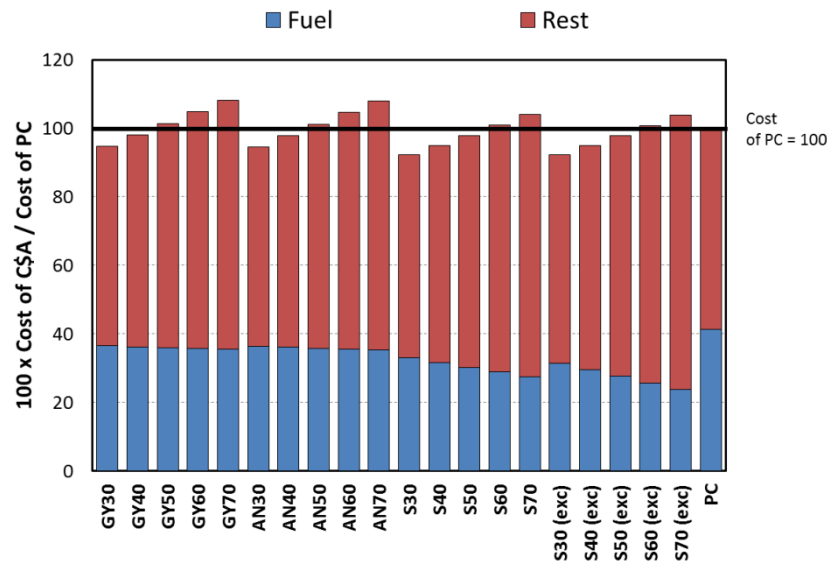


348

349 **Figure 3. Tornado chart showing the influence of the certain assumptions in the calculation of GHG emissions for C\$A**  
 350 **clinker manufacturing**

### 351 3.2. Economics of production of 1 tonne of C\$A clinker

352 With regards to costs, the main results for the assumed scenarios are shown in Figure 4 relative to the cost of PC.  
 353 Costs seem to be negatively influenced by compositions higher in ye'elinite as they require a higher amount of  
 354 bauxite in the raw meal. The economic performance can be optimised if the amount of bauxite fed to the process is  
 355 kept at a minimum value. The use of alternative raw materials with high Al<sub>2</sub>O<sub>3</sub>, such as high-alumina clays, is an  
 356 option which has already been proven experimentally (Hanein et al, 2016b); however, costs, availability, and  
 357 geographic distribution would require a deeper analysis. Fuel costs are reduced for all C\$A options and are further  
 358 reduced in cases of sulfur combustion.



359

360

**Figure 4. Costs of C\$A clinker manufacturing in relation to PC, low-cost bauxite**

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365

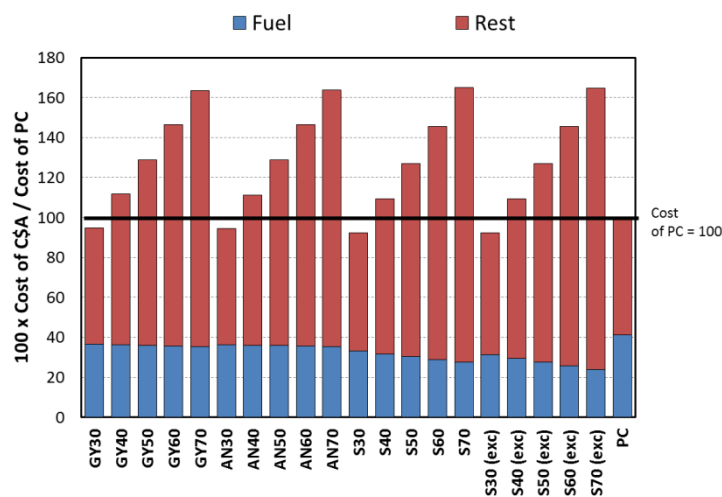
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369

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 IAI, 2013, 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 IAI 2013, has a significant negative impact on the economy of high-ye'elinite C\$A as demonstrated in Figure 5. While all C\$A formulations appear to reduce the emissions from PC independently of the content of ye'elinite, the cost of bauxite has a key influence on the economic optimum of ye'elinite content. A high ye'elinite clinker can cost 60% more than PC in the worst-case scenario of bauxite shipping costs.



370

371

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

372

373

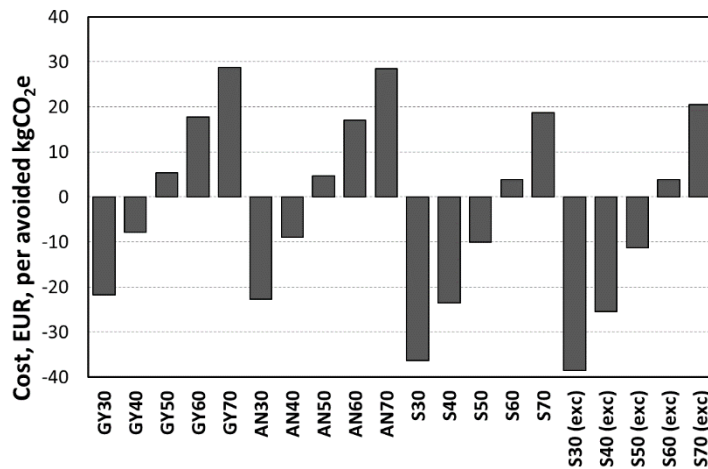
374

375

In all cases, the C\$A costs are heavily dependent on the content of ye'elinite 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'elinite, 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<sub>2</sub> by switching from PC to C\$A



376 has been calculated as the variation of costs divided by the variation of emissions (see Figure 6) from PC for each  
 377 C\$A clinker (the lower cost estimate of bauxite is used).



378

379 **Figure 6. Cost per avoided tonne of CO<sub>2</sub> from C\$A cement manufacturing in relation to PC manufacturing when the**  
 380 **lower cost estimate of bauxite is used.**

381 As observed in Figure 6, higher ye'elinite contents yield higher CO<sub>2</sub> avoidance costs. The negative value of this cost  
 382 indicates savings brought about by using C\$A cement as an alternative to PC. The use of sulfur produces a lower  
 383 cost of avoidance than any option using gypsum, as is expected from the lower theoretical heat, and the amount of  
 384 compensated heat from natural gas produces more savings than the higher associated emissions of sulfur in  
 385 comparison to gypsum or anhydrite.

#### 386 4. Discussion

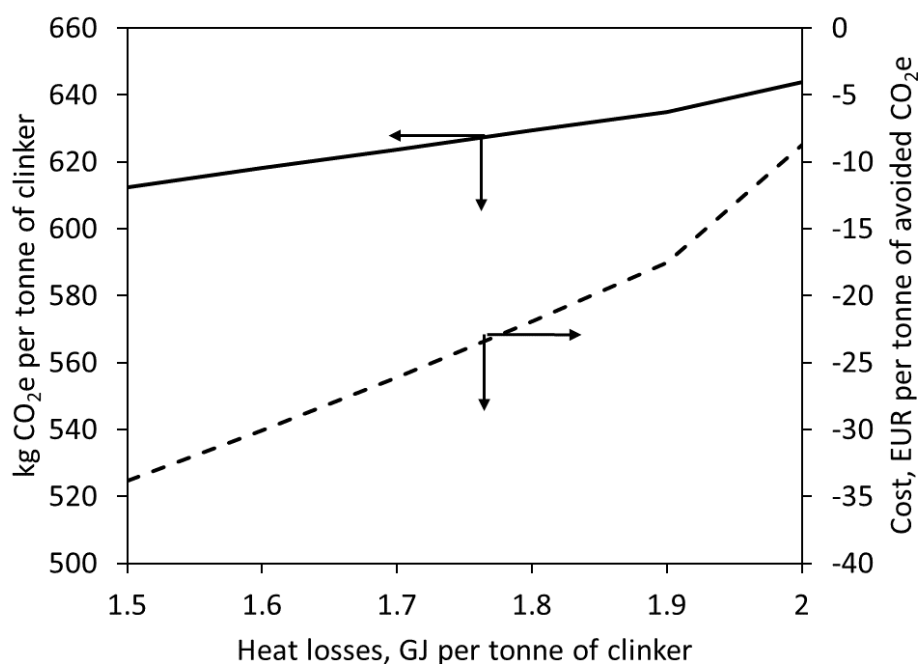
387 This systematic study has shown that C\$A clinker formulations based on ye'elinite, can have a lower carbon footprint  
 388 than PC while remaining cost competitive under certain (but not unusual) economic conditions. As C\$A requires a  
 389 higher content of sulfur fed in the raw meal this can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

397 In general, the production of C\$A clinker requires less energy than ordinary PC. The lower theoretical heat  
 398 requirements for C\$A production are reflected in the calculations shown above; however, no changes are assumed  
 399 for the thermal efficiency of the kiln, which is assumed the same for C\$A and PC. As explained, heat losses are  
 400 assumed to be around 2GJ per tonne of clinker for both, but it is suspected to be lower in efficient modern kilns  
 401 operating at lower burning temperature. If the gas mixture exhaust of PC clinker production, as described by the  
 402 European Commissions' best available techniques reference document (EC, 2013) for the cement industry is used



403 (21%CO<sub>2</sub>, 12.3% O<sub>2</sub>, 62%N<sub>2</sub>, H<sub>2</sub>O 4%) and the temperature is reduced from 1450°C to 1250°C, a saving in sensible  
 404 heat of 1GJ per tonne of clinker would be achievable. However, main heat losses due to radiation and also those at  
 405 the lower temperature end of the kiln are difficult to estimate.

406 To illuminate the effects of a better kiln efficiency, the influence of the heat losses on the carbon footprint and cost  
 407 of C\$A clinker with 50% ye'elimite produced with sulfur is shown in Figure 7. It is observed that the variation in  
 408 emissions is not as significant as the influence on costs. Carbon dioxide emissions from C\$A production vary from  
 409 610 to 644 kg CO<sub>2</sub>e per tonne of clinker (a 5% maximum variation), while the cost of CO<sub>2</sub> avoidance increases  
 410 significantly, i.e. more than 70%, as the efficiency decreases. In the example of Figure 7, negative costs indicate  
 411 savings in comparison to PC that are improved when the efficiency of the kiln is higher. This means that higher  
 412 operational expenses from more expensive raw materials might be compensated by the improved thermal efficiency  
 413 in a modern C\$A clinker production facility.



414

415 **Figure 7. Influence of kiln heat losses on the carbon footprint (solid) and cost per tonne of avoided CO<sub>2</sub>e (dashed) for**  
 416 **C\$A clinker with 50% ye'elimite produced by burning stoichiometric sulfur.**

417 Another interesting aspect is the source of sulfur. Elemental sulfur is assumed to be sourced from the desulfurisation  
 418 of fossil fuels. Although it may be thought of as a waste, it is defined as a product due to its usually high quality,  
 419 wide market, and relative high demand; thus, the associated emissions and a price are assumed in this work. In the  
 420 case of calcium sulfate, it can be sourced from a natural origin, but it can also be sourced from wasted plasterboard  
 421 and, especially, as a by-product from the desulfurisation of flue gases in power plants. It shall be considered a waste:  
 422 the producer wants to dispose of it, and its demand as secondary material does not cover the whole production of this  
 423 so-called “waste”. The associated supply chain emissions of the calcium sulfate “waste” are null (except for the  
 424 transportation to the cement production site). Therefore, calcium sulfate wastes can be preferred against elemental  
 425 sulfur according to the sensitivity analysis performed in this work; a 50% ye'elimite C\$A clinker tonne has a carbon  
 426 footprint of 595 kg CO<sub>2</sub>e if produced from natural gypsum, 644 kg CO<sub>2</sub>e if elemental sulfur is used, and would have  
 427 only 588 kg CO<sub>2</sub>e if recycled calcium sulfate is used.

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

439 The results presented here demonstrate that the source of alumina is critical to the economic performance of the  
440 process. Al<sub>2</sub>O<sub>3</sub> can be supplied from high alumina clays and the economics of using clays are more favourable than  
441 situations where the raw feed includes sources of bauxite; however, the analysis performed only considers marginal  
442 changes, i.e. the production of C\$A cement does not impact the economic system. It is envisaged that mass production  
443 of C\$A cements would have an enormous impact on the economics of bauxite sourcing. Probably, the higher demand  
444 on a resource such as bauxite, only available in specific geographical locations, would generate a serious limitation  
445 on the commercialisation of low-carbon C\$A cements.

446 Due to the substantial reduction in CO<sub>2</sub> emissions offered by C\$A clinker compared to PC clinker, carbon taxation  
447 is another aspect which could significantly sway the course of commercial cement manufacture in favour of C\$A in  
448 the near future. A number of countries have already implemented CO<sub>2</sub> taxation (notably not yet the USA and China)  
449 and the cost of emitting CO<sub>2</sub> is increasing. Further CO<sub>2</sub> taxation increases are expected as it is foreseen to be one of  
450 the major drivers of the Paris Agreement (UN, 2015) within the United Nations Framework Convention on Climate  
451 Change that went into action in November 2016 and will start tackling GHG mitigation in 2020.

## 452 5. Conclusions

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

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

461 The introduction of bauxite as raw material for cement has a significant influence on costs, but this study demonstrates  
462 a significant potential for optimisation, e.g. the raw materials, the ye’elimite content of the clinker, the energy  
463 performance of the kiln, and the probable suitability of sulfur-bearing fossil fuels. If relatively cheap sources of

464 aluminium oxide can be found and no deep modifications of the kiln technology are required, current production  
 465 costs are competitive and CO<sub>2</sub> avoidance costs are negative for the cement industry, suggesting that low CO<sub>2</sub> cement  
 466 clinker production is also economically preferable.

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