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# 1 Production and hydration of calcium sulfoaluminate-belite 2 cements derived from aluminium anodising sludge

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## 15 Abstract

16 Calcium sulfoaluminate-belite cement (CSAB) offers lower CO<sub>2</sub> emissions in its  
17 production, compared with Portland cement. However, for the production of CSAB a  
18 high amount of alumina is required, and the scarcity and high cost of high-purity  
19 bauxite make these cements costly at present. In this study, the use of uncalcined  
20 aluminium anodising sludge (AAS) as the main source of alumina to produce CSAB  
21 clinkers, replacing bauxite, was assessed. The CSAB clinkers produced were mainly  
22 composed of ye'elinite and belite, along with minor traces of alite, and/or  
23 brownmillerite, depending on the alumina source. Clinkers derived from AAS as a  
24 source of aluminium showed a lower content of ye'elinite (35.5%), as well as the

25 formation of alite (8.2%) when compared to a reference clinker produced with reagent-  
26 grade materials. Comparable hydration products were identified in the hydrated cements  
27 independent of the alumina source used. The use of AAS to produce CSAB cement was  
28 proven to be technically feasible, and the cement thus produced has desirable technical  
29 characteristics, presenting high mechanical strength (>40 MPa in paste samples).

30 **Keywords:** Calcium sulfoaluminate cement; clinker; hydration; anodising  
31 sludge; waste valorisation.

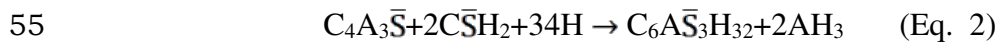
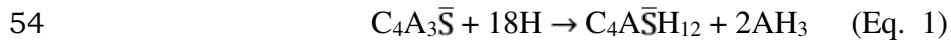
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### 33 1. Introduction

34 Calcium sulfoaluminate (CSA) cements are based on the hydraulic phase  
35 tetracalcium trialuminate sulfate ( $C_4A_3\bar{S}$  in cement chemistry notation), also known  
36 by the mineral name ye'elimite, as a major constituent [1–4]. As minor  
37 constituents, belite ( $C_2S$ ), tricalcium aluminate ( $C_3A$ ), calcium sulfosilicates  
38 (sulfospurrite or ternesite,  $C_5S_2\bar{S}$ ), Al-rich ferrite ( $C_4AF$ ) and calcium silico-  
39 aluminates (e.g. gehlenite,  $C_2AS$ ) can also be present in these clinkers [5–7]. When  
40 the composition of the raw materials, the raw mix design or the clinkering  
41 processes change, some clinkers with different chemical and mineral compositions  
42 can also be generated, e.g. calcium-sulfoaluminate-belite (CSAB) cements  
43 containing mainly  $C_4A_3\bar{S}$  and belite [3,8]; belite-rich cements containing both  
44 calcium sulfoaluminate and ferrite phases [8–12]; belite calcium-sulfoaluminate-  
45 ternesite cement [13,14], among others. The main difference between these cements  
46 and Portland cement (PC) is the low concentration or absence of tricalcium silicate  
47 ( $C_3S$ , alite) in CSA based clinker, and its higher content of sulfates.

48 Glasser and Zhang [15] proposed a hydration model for calcium sulfoaluminate binders.  
49 The high reactivity of  $C_4A_3\bar{S}$  with calcium sulfates and water leads to rapid setting and

50 formation of ettringite ( $C_6A\bar{S}_3H_{32}$ ), calcium monosulfoaluminate hydrate ( $C_4A\bar{S}H_x$   
51 where  $x$  is approximately 10-19; often termed  $SO_4$ -AFm or ‘monosulfate’), and  
52 amorphous aluminium hydroxide ( $AH_3$ ) (Eq. 1 and 2, respectively) as the main  
53 hydration products, which contribute to high early strength [16].



56 The relative quantities of ettringite and  $SO_4$ -AFm formed are related to the ratio of  
57 sulfate to aluminate present during the reaction. Other hydrate products identified  
58 include additional AFm-type phases (calcium carboaluminate hydrates or strätlingite),  
59 and hydrogarnet-type phases (mainly siliceous hydrogarnet) [1,16–20]. The  
60 understanding of the hydration mechanism and products of CSA cements have been  
61 advanced by Winnefeld and Lothenbach [17] through thermodynamic modelling,  
62 predicting the formation of ettringite and amorphous  $Al(OH)_3$  from the hydration of  
63 ye’elimite. As the content of calcium sulfate decreases, monosulfate forms, along with  
64 the depletion of Ca and sulfate. If belite is present (as in CSAB cements), strätlingite is  
65 also formed as a secondary hydrate product [17].

66 The main applications for CSA-based cement, or its blends with Portland cement  
67 (PC), are in the production of self-stressed concrete elements, high early strength  
68 concretes for pre-cast products, cold weather concrete products, glass-fibre-  
69 reinforced composites and self-levelling floors [21,22]. CSA-based cement has  
70 been also used for the immobilisation of hazardous materials due to its low  
71 permeability and dense structure when hydrated [23].

72 CSA-based clinkers are generally produced by calcination of limestone, bauxite and  
73 gypsum, under conditions tailored to yield a desirable composition of the final

74 clinker [8,24]. These cements may be considered as a more sustainable alternative  
75 to PC due to the lower energy consumption and reduced CO<sub>2</sub> emissions associated  
76 with their production, as a result of the reduced limestone content required  
77 compared to PC [24]. CSA-based cements only release 0.216 g of CO<sub>2</sub>/mL of the  
78 cementing phase, which is considerably lower than alite-based cements, the  
79 production of which emits 0.578 g of CO<sub>2</sub>/mL [3]. The temperature of calcination is  
80 also around 200 °C lower than is commonly used for PC production [14,25]. The  
81 low energy required for its grinding process, due to the friable clinker [4,14], also  
82 reduces the energy necessary for producing CSA-based cements [26,27].

83 CSA-based cement has been manufactured and successfully used since the 1970s in  
84 China, and also produced on a more limited scale in the E.U. and the U.S. [1,28].  
85 Although in the past its worldwide production was relatively small, more recently  
86 major international companies have developed new products. For example, some  
87 industrial organisations are presenting new CSA cements based on recycled  
88 materials [29], and a new generation of low-carbon belite-rich sulfoferroaluminate  
89 cements has been patented under the name AETHER<sup>®</sup> [30], with a reduction of 25-  
90 30% in the emissions of CO<sub>2</sub> per tonne of cement when compared to PC. Various  
91 belite calcium sulfoaluminate ternesite (BCT) cements have also been patented  
92 since 2011 [31].

93 With a global production of 234 M metric tonnes annually [32], bauxite is a valuable  
94 resource for many industries, mainly for the production of alumina for manufacturing of  
95 aluminium metal. Global bauxite resources are estimated to be 55 to 75 billion tonnes,  
96 which are distributed in Africa (32%, Oceania (23%), South America and the Caribbean  
97 (21) and Asia (18%) [33]. Even though there exist relatively abundant available sources,  
98 the high demand for bauxite, as well as the costs related to its transport, reduce its

99 economic viability as a raw material for the manufacture of cements. This elucidates the  
100 challenges facing its potential use as a raw material in the production of CSA clinkers.  
101 Therefore, there is an imminent need to seek alternative alumina sources, such as Al-  
102 rich wastes or industrial by-products, to enable the cost-competitive production of these  
103 cements. Different industrial wastes or by-products with high contents of CaO, SO<sub>3</sub>,  
104 and Al<sub>2</sub>O<sub>3</sub>, including fly ashes, blast furnace slag, phosphogypsum wastes,  
105 galvanising sludge, baghouse ash, and red mud have been used for the laboratory  
106 production of CSAB clinkers [9,24,34–38].

107 Aluminium anodising sludge (AAS) is an industrial waste produced during the  
108 electrochemical process of anodising aluminium. The solid waste obtained from this  
109 process is a sludge with a high content of aluminium hydroxide (Al(OH)<sub>3</sub>), and other  
110 compounds including aluminium sulfate, sodium or calcium hydroxide can also be  
111 present. According to the Brazilian standard ABNT NBR 10004:2004 [39], this waste  
112 can be considered as a non-hazardous material, and it has been used as a source of  
113 Al<sub>2</sub>O<sub>3</sub> in the production of mullite-based ceramics [40,41]. The high amounts of this  
114 waste produced (100 kt/year in the EU and ~1500 kt/y in Brazil), and the lack of a full  
115 pathway for its re-use, raise environmental concerns [42]. The assessment of AAS as a  
116 raw material for the production of a belitic cement (without the presence of ye'elimite-  
117 type phases) was previously reported by Pereira *et al* [43,44], but the use of AAS as a  
118 source of Al<sub>2</sub>O<sub>3</sub> in the synthesis of CSAB-type cement (whose clinker contains belitic  
119 and ye'elimite phases) has not been studied. Therefore, it is not fully understood  
120 whether the differences between chemical compositions and presence of minor elements  
121 between bauxite and AAS will have a significant effect during the synthesis of CSAB-  
122 type cements, and the hydrated products formed from the clinkers derived from this  
123 waste have not been assessed in detail.

124 The aim of this study is to assess the potential use of an aluminium anodising sludge as  
125 an alternative source of  $\text{Al}_2\text{O}_3$ , instead of bauxite, in the production of CSAB clinkers.  
126 The effect of partial and total substitution of bauxite by AAS on the final phase  
127 assemblage obtained during the synthesis of CSAB clinkers were assessed, to identify if  
128 the use of alternative sources of  $\text{Al}_2\text{O}_3$  during the synthesis modifies the clinker phase  
129 assemblages formed. The hydration products formed from these clinkers were also  
130 assessed using X-ray diffraction (XRD), thermogravimetric analysis (TGA) and  $^{29}\text{Si}$  and  
131  $^{27}\text{Al}$  solid state magic angle spinning nuclear magnetic resonance spectroscopy (MAS-  
132 NMR). The hydration kinetics were studied through isothermal conduction calorimetry  
133 (ICC), and the compressive strength development during curing was also determined.

## 134 2. Experimental Procedure

### 135 2.1. Materials

136 For the production of the CSAB clinkers two different sources of alumina were used: an  
137 aluminium-anodising sludge with 70.0%  $\text{H}_2\text{O}$  supplied by Alcoa (Tubarão, Brazil), and  
138 a bauxite-rich mineral from Curimbaba (São João Del Rei, Brazil). Limestone was  
139 supplied by Cimpor Cement (Candiota, Brazil). The other raw materials, used mainly  
140 for sintering the reference clinker, were analytical grade:  $\text{CaCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  
141  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , and  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$  supplied from Dinâmica Contemporânea Ltda. The  
142 chemical compositions of the raw materials are shown in Table 1.

143

144

145

146

147 Table 1 Chemical compositions of raw materials used (wt.%, from X-ray fluorescence)

Raw Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Cl <sup>-</sup>	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI*	Other
Calcium sulfate <sup>†</sup>	--	--	--	46.4	32.5	-	--	--	--	--	--	21.1	-
Silicon oxide <sup>†</sup>	83.6	-	-	-	-	-	-	-	-	-	-	16.4	-
Ferric oxide <sup>†</sup>	--	--	96.5	--	--	--	--	--	--	--	--	3.5	--
Aluminium oxide <sup>†</sup>	-	96.5	-	-	-	-	-	-	-	-	-	3.5	-
Calcium carbonate <sup>†</sup>	-	-	-	-	56.0	-	-	-	-	-	-	44.0	-
Limestone	12.9	2.3	1.4	0.1	41.2	4.0	-	0.7	-	0.1	0.2	37.0	0.3
Bauxite (Bx)	10.0	75.0	12.7	-	-	0.1	-	0.2	-	1.1	0.1	0.2	0.6
Aluminium anodising sludge (AAS)**	1.9	73.6	0.5	20.5	0.6	0.2	1.2	0.2	0.1	-	0.5	-	0.7

148 <sup>†</sup>Analytical grade    \*Loss on ignition at 1050 °C.    \*\*Dried at 100 °C for 24 h

149

150 2.2. *Synthesis of CSAB clinker*

151 The CSAB clinkers were formulated according to the Bogue-type equations procedure  
 152 suggested by Majling *et al.* [45], with the raw meal mixes designed to obtain similar  
 153 oxide compositions and a phase assemblage based on 40% C<sub>2</sub>S, 40% C<sub>4</sub>A<sub>3</sub> $\bar{S}$ , 10% C<sub>4</sub>AF  
 154 and 10% C $\bar{S}$ , while other minor clinker phases are predicted to be negligible [24,25].  
 155 The proportions of the raw materials, and clinker IDs, are shown in Table 2. The  
 156 reference clinker (CSAB-Ref) was formulated and produced with reagent grade  
 157 materials. Total and partial substitution of bauxite by AAS was carried out in order to  
 158 assess the effect of Al<sub>2</sub>O<sub>3</sub> source on the final properties of the clinker produced.

159 Table 2 Formulations used for the synthesis of CSAB clinkers (wt.%)

Raw Materials	Clinker ID		
	CSAB-Ref	CSAB-Bx/AAS	CSAB-AAS
Calcium carbonate (reagent grade)	51.1	1.1	-
Calcium sulfate (reagent grade)	17.5	11.9	7.3
Aluminium oxide (reagent grade)	16.8	-	-
Silicon oxide (reagent grade)	12.2	-	0.2
Ferric oxide (reagent grade)	2.5	-	1.1

Limestone	-	68.6	72.9
Bauxite (Bx)	-	9.2	-
Aluminium anodising sludge (AAS)*	-	9.2	18.5

160 \*Dried at 100 °C for 24 h

161

162 The raw materials (100% passing 75 µm) were dried at 100 °C for 24 h, homogenised  
163 using a ball mill for 1 h (balls:powder mass ratio 1:5, 60 rpm) and then pelletised  
164 (moulded manually into spherical pellets with a moisture content of 30% and diameter  
165 ~1 cm). After drying in an oven (100 °C for 24 hours) the pellets were heated at 900 °C  
166 for 30 min and then sintered at 1250 °C for 30 min in a static laboratory muffle furnace  
167 with a heating rate of 5 °C/min, followed by quenching with forced air convection. The  
168 clinkers were then ball milled and sieved to 100% passing 45 µm.

169 The particle size distributions of the ground clinkers were analysed using a laser  
170 granulometer 1180 (CILAS). Mineralogy was analysed by X-ray diffraction using a  
171 PANalytical Empyrean diffractometer with Cu K $\alpha$  ( $\lambda=1.5418$  Å) radiation, a step size  
172 of 0.013°, 97.92 s count time per step (~30 min data collection per scan). Quantitative  
173 analysis was performed through Rietveld analysis using the X'Pert High Score Plus  
174 software (PANalytical), with goodness-of-fit calculated to be better than 3.3 and  
175 Weighted R profile maximum 7.3%. Structural data for alite [46], belite [47], ferrite  
176 [48], cubic ye'elimite [49], orthorhombic ye'elimite [50], ternesite [51], anydrite [52],  
177 and periclase [53] were used for refinement and quantification of the anhydrous  
178 crystalline phases. X-ray fluorescence data were collected using an Axios Advanced  
179 spectrometer (PANalytical) via standardless semiquantitative analysis. Loss on ignition  
180 was performed at 1050 °C for 1 h in air.

181 2.3. *Tests conducted on pastes*

182 Pastes using the three CSAB clinkers synthesised (CSAB-Ref; CSAB-Bx/AAS; and  
183 CSAB-AAS) were produced with a water/binder ratio of 0.45, following Chen and  
184 Juenger [25] and Jewell *et al.* [54]. The hydration process of the CSAB clinkers was  
185 assessed by isothermal conduction calorimetry using a TAM Air calorimeter (TA  
186 Instruments). The mixtures were hand mixed for 5 min and then placed into the  
187 calorimeter. The heat evolution was evaluated for 24 h at 23 °C.

188 The compressive strength development was assessed in 13 mm cubic paste samples,  
189 cured under saturated limewater at 25 °C due to the high content of belite in the clinker.  
190 The compressive strength was determined after 3, 7, and 28 of curing according to the  
191 method proposed by Mehta and Gjorv [55], using a universal testing machine UH-  
192 F2000KN (Shimadzu) with a loading rate of 0.2 MPa/s. The results reported correspond  
193 to the mean of four replicate samples tested for each formulation.

194 The hydrated samples were crushed, treated with isopropanol to prevent further  
195 hydration, filtered, and stored in a sealed container until testing. The hydration products  
196 were evaluated through:

- 197 - X-ray diffraction (XRD), as described for the anhydrous clinker phases above.
- 198 - Thermogravimetric analysis using a Mettler Toledo TGA/TSO SDTA 851e, under a  
199 flow rate of 40 mL/min of nitrogen and a heating rate of 10 °C/min up to 1000 °C.
- 200 - Solid-state <sup>29</sup>Si MAS NMR; spectra were collected at 59.56 MHz on a Varian Unity  
201 Inova 300 (7.05 T) spectrometer using a probe for 7.5 mm o.d. zirconia rotors and a  
202 spinning speed of 5 kHz. The <sup>29</sup>Si MAS experiments employed a 90° pulse of duration  
203 5 μs, a relaxation delay of 5 s and 14000 scans. Solid-state <sup>27</sup>Al MAS NMR spectra  
204 were acquired at 104.198 MHz, using a Varian VNMRS 400 (9.4 T) spectrometer and  
205 a probe for 4 mm o.d. zirconia rotors and a spinning speed of 14 kHz with a pulse

206 width of 1  $\mu$ s (approximately 25°), a relaxation delay of 0.2 s, and a minimum of 7000  
207 scans.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  chemical shifts are referenced to external samples of  
208 tetramethylsilane (TMS), and a 1.0 M aqueous solution of  $\text{Al}(\text{NO}_3)_3$  respectively.

### 209 3. Results and Discussion

#### 210 3.1. Characterisation of CSAB clinkers

211 The chemical compositions, obtained by XRF, of the clinkers produced are shown in  
212 Table 3. The contents of  $\text{CaO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SO}_3$ , and  $\text{Fe}_2\text{O}_3$  in the CSAB clinkers after  
213 sintering were similar for all samples, and the XRD phase quantification shows that the  
214 clinkers were close to the target phase compositions (Table 4 and discussion below).  
215 These results elucidate the effectiveness of the use of the Bogue method as modified by  
216 Majling *et al.* [56] in designing CSAB clinkers using different raw materials. The slight  
217 deviations can be attributed to the impurities contained in the mineral and waste  
218 materials. The higher content of  $\text{MgO}$  of the clinkers produced with the alternative  
219 alumina sources (CSAB-Bx/AAS and CSAB-AAS) can be attributed to the use of  
220 limestone with an  $\text{MgO}$  content higher than 5 wt.% (Table 1). The content of  $\text{Na}_2\text{O}$  and  
221  $\text{K}_2\text{O}$  is also higher, especially for CSAB-AAS, due to the alkalis supplied by the AAS.  
222 Table 3. Chemical compositions of CSAB clinkers produced (wt.%).

Compound	CSAB-Ref	CSAB-Bx/AAS	CSAB-AAS
CaO	48.9	49.8	51.2
Al <sub>2</sub> O <sub>3</sub>	16.9	16.0	15.1
SiO <sub>2</sub>	16.8	11.1	9.7
SO <sub>3</sub>	12.4	10.9	12.1
Fe <sub>2</sub> O <sub>3</sub>	3.7	3.7	3.3
MgO	0.1	5.6	5.1
Na <sub>2</sub> O	0.4	0.4	0.8
K <sub>2</sub> O	0	0.7	0.7
Cl	0.03	0.02	0.02
TiO <sub>2</sub>	0	0.40	0.1
P <sub>2</sub> O <sub>5</sub>	0.02	0.1	0.1
Other components	0.18	0.40	0.29
LOI*	0.57	0.78	1.48

223

\*Loss on ignition at 1050 °C for 1 h.

224 The X-ray diffraction patterns of the anhydrous CSAB clinkers (Figure 1) and their  
 225 corresponding results of Rietveld quantitative phase analysis (Table 4) show the  
 226 presence of ye'elimite (both cubic and orthorhombic polymorphs, Ca<sub>3</sub>Al<sub>6</sub>O<sub>12</sub>·CaSO<sub>4</sub>,  
 227 Powder Diffraction File (PDF) cards # 01-071-0969 and # 01-085-2210, respectively)  
 228 and belite (Ca<sub>2</sub>SiO<sub>4</sub>; PDF# 01-086-0398). The absence of free lime indicates a complete  
 229 conversion to the CSAB clinker phases, when either reagent-grade raw materials,  
 230 natural (Bx), or waste materials (AAS) were used. Ternesite (Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>); PDF#  
 231 01-088-0812), anhydrite (CaSO<sub>4</sub>; PDF#00-003-0162), a substituted aluminoferrite-type  
 232 phase (brownmillerite-type structure, approximated for brevity as C<sub>4</sub>AF), PDF# 01-087-  
 233 1229) and alite (3CaO·SiO<sub>2</sub>, PDF# 01-086-0402), were identified. Periclase (MgO,  
 234 PDF# 00-003-0998) was observed only in the CSAB-Bx/AAS and CSAB-AAS  
 235 clinkers. The formation of alite can be attributed in part to the presence of MgO in the  
 236 limestone [57], which was only used for the synthesis of the CSAB-Bx/AAS and  
 237 CSAB-AAS clinkers. Liu *et al.* [57] reported that the presence of a suitable amount of

238 MgO (>0.5%) can promote the formation of C<sub>3</sub>S at lower temperatures and is beneficial  
239 for its coexistence with C<sub>4</sub>A<sub>3</sub> $\bar{S}$ . The higher content of P<sub>2</sub>O<sub>5</sub> in the raw meal mixes used  
240 for the production of CSAB-Bx/AAS and CSAB-AAS might have an effect on the  
241 synthesis of C<sub>2</sub>S, C<sub>3</sub>S and C<sub>4</sub>A<sub>3</sub> $\bar{S}$ . The stabilization of  $\beta$ -C<sub>2</sub>S has been identified,  
242 indicating that the clinkering and cooling processes were properly performed [58,59].  
243 Traces of calcite (CaCO<sub>3</sub>; PDF# 00-002-0623) are also identified, as a consequence of  
244 possible carbonation of the samples during storage and analysis.

245 The percentages of the main clinker phases (C<sub>4</sub>A<sub>3</sub> $\bar{S}$ , C<sub>2</sub>S and C<sub>4</sub>AF) are very similar to  
246 the expected values from the Bogue-type calculations. The CSAB-Ref exhibited a  
247 higher amount of ye'elimite (the sum of the orthorhombic and cubic structures) than the  
248 other CSAB clinkers. However, as the content of AAS used in the production of CSAB  
249 increases, the ratio of orthorhombic to cubic ye'elimite is also higher. CSAB-Ref  
250 showed the lowest cubic-C<sub>4</sub>A<sub>3</sub> $\bar{S}$ /orthorhombic-C<sub>4</sub>A<sub>3</sub> $\bar{S}$  ratio (0.094) when compared to the  
251 CSAB clinkers derived from AAS (0.20 and 0.23 for CSAB-Bx/AAS and CSAB-AAS,  
252 respectively). Bullerjahn *et al.* [14] reported a higher content of cubic ye'elimite at the  
253 expense of the orthorhombic form with increasing Fe content. Although the differences  
254 in iron content between the clinkers CSAB-Ref and CSAB-Bx/AAS appear negligible,  
255 the crystallisation of the cubic polymorph might be promoted by the presence of foreign  
256 ions, including Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ti<sup>4+</sup>, which are present in higher concentrations in  
257 CSAB-Bx/AAS clinker, Table 3. Hargis *et al.* (2014) [60] identified, using Rietveld  
258 refinements for cubic, orthorhombic, and tetragonal crystals, that the peak intensities  
259 and positions of the orthorhombic crystal structure best match pure C<sub>4</sub>A<sub>3</sub> $\bar{S}$

260

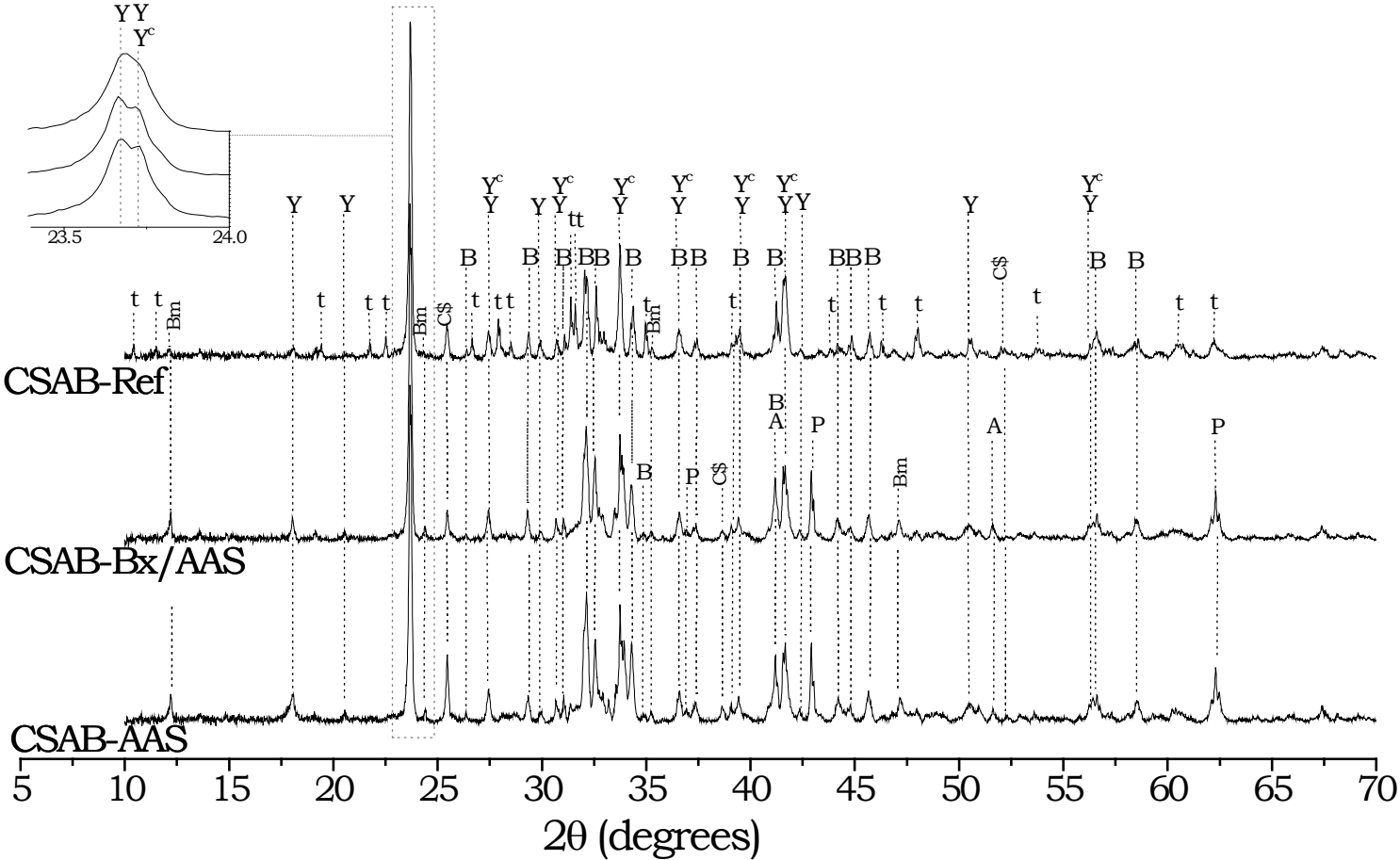
261 Table 4. Rietveld quantitative phase composition of the CSAB clinkers produced.

262 Values reported in mass percentages

	CSAB-Ref	CSAB-Bx/AAS	CSAB-AAS
Orthorhombic ye'elimite ( $C_4A_3\bar{S}$ )	37.0	25.5	28.8
Cubic ye'elimite ( $C_4A_3\bar{S}$ )	3.5	5.3	6.7
Total ye'elimite (cubic + orthorhombic)	40.5	30.8	35.5
Belite ( $C_2S$ )	32.1	41.1	39.1
Ternesite ( $C_5S_2\bar{S}$ )	19.3	--	--
Brownmillerite-type phases ( $C_4AF$ )	4.6	11.9	7.4
Anhydrite ( $C\bar{S}$ )	3.5	2.0	4.0
Alite ( $C_3S$ )	--	7.7	8.2
Periclase (MgO)	--	6.5	5.9
Agreement indices			
R expected - $R_{exp}$ (%)	4.1	4.1	4.1
Weighted R profile - $R_{wp}$ (%)	7.3	6.0	6.4
Goodness of fit - $\chi^2 = \left[ \frac{R_{wp}}{R_{exp}} \right]^2$	3.2	2.2	2.4

\*Loss on ignition at 1050 °C.

263  
264



Y: orthorhombic ye'elimite; Y<sup>c</sup>: cubic ye'elimite; B: belite; t: ternesite; Bm: brownmillerite; C\$: anhydrite; A: alite; P: periclase

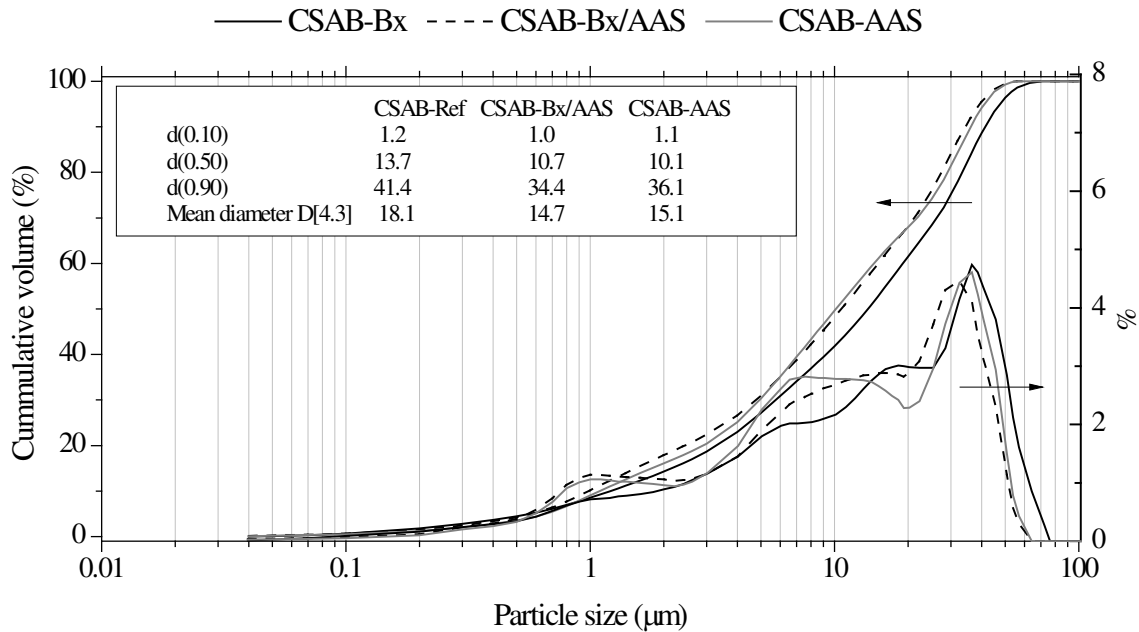
Figure 1. X-ray diffractograms of anhydrous CSAB clinkers

265  
266  
267

268 A calcium sulfosilicate with a ternesite-type structure ( $\text{Ca}_5(\text{SiO}_4)_2(\text{SO}_4)$ ;  $\text{C}_5\text{S}_2\bar{\text{S}}$ ) was  
269 identified only in CSAB-Ref, which also has the lowest  $\text{C}_4\text{AF}$  and  $\beta\text{-C}_2\text{S}$  contents.  
270 Ternesite is an intermediate phase generally present at temperatures between 1100 and  
271 1180 °C during the crystallisation of belite in CSAB cements, whose formation is  
272 strongly affected by the content of  $\text{SO}_3$ , the presence of mineralisers (including  
273 phosphates or fluorides) and/or the cooling rate from 1250 to 800 °C [14,61]. Taking  
274 into account that quenching from ~1200 °C was applied after clinkerisation, and that the  
275 contents of  $\text{SO}_3$  among the clinkers assessed here are similar, the sulfate supplied by the  
276 AAS (which is ~20%, Table 1) might have higher availability during the synthesis than  
277 the sulfate provided as anhydrite. The minor oxides ( $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ ) supplied by the  
278 limestone, bauxite and AAS promoted the formation of alite in CSAB-Bx/AAS and  
279 CSAB-AAS. Ternesite formation occurred under conditions of the absence of such  
280 mineralizing elements and higher availability of  $\text{SiO}_2$ .

281 The particle size distributions of the CSAB clinkers obtained after mechanical treatment  
282 do not exhibit significant differences, Figure 2.

283



284

285

Figure 2. Particle size distributions of CSAB clinkers.

286 *3.2. Phase evolution during hydration of CSAB clinkers*

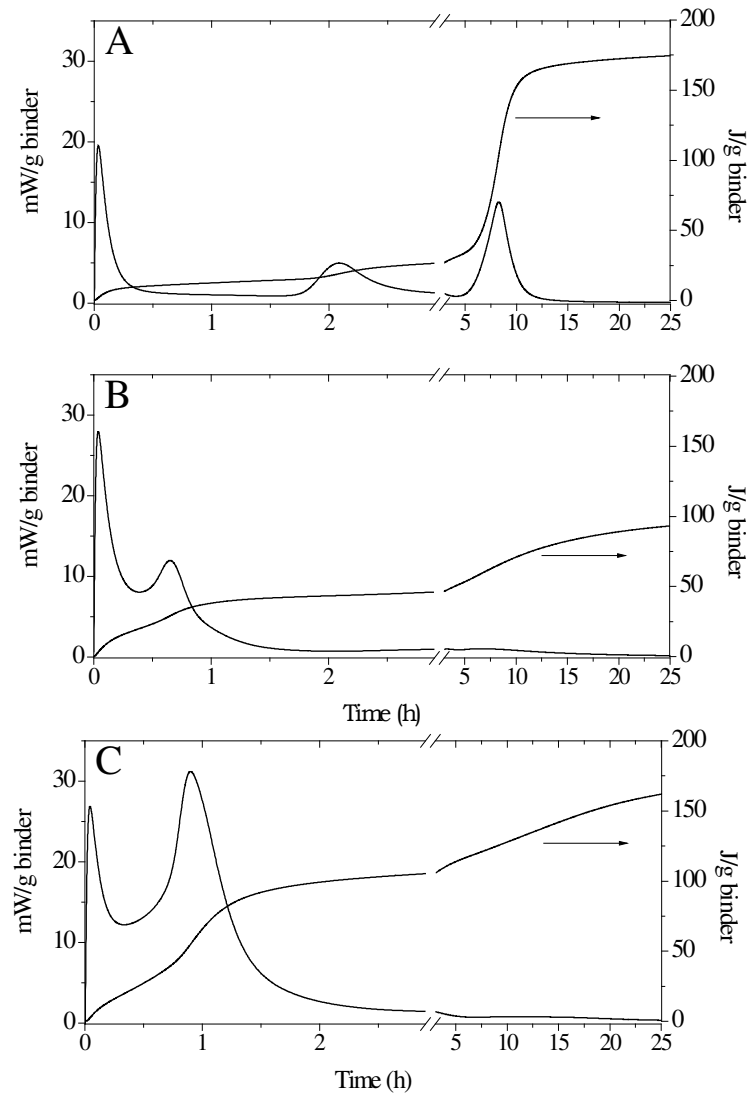
287 *3.2.1. Isothermal calorimetry*

288 The heat release profiles during the hydration of the clinkers show two distinct peaks  
 289 (Figure 3); the first appears during the initial five minutes of reaction and the second is  
 290 after 0.5-2 hours. CSAB-Ref showed a third peak after 8 h (Figure 3A), which is  
 291 tentatively attributed to the formation of additional ettringite as hydration continues, but  
 292 this was not observed for the other clinkers (Figure 3B,C).

293 The CSAB-Bx/AAS and CSAB-AAS clinkers show the highest heat release rate during  
 294 initial hydration (~27 mW/g binder), 2 minutes after loading into the calorimeter (7  
 295 minutes after the start of mixing), followed by CSAB-Ref, although the data obtained  
 296 during this very early period must be treated as semi-quantitative due to the requirement  
 297 for stabilisation of the calorimeter after loading. The second peak located after ~1 h for  
 298 CSAB-AAS is more intense (maximum heat evolution rate 31 mW/g binder) compared  
 299 with the corresponding peak for CSAB-Bx/AAS, which is present at 40 min and with

300 lower intensity (maximum rate 12 mW/g binder). Considering that the clinkers showed  
301 similar particle size distributions (Figure 2), the effect of fineness on the differences  
302 identified in the hydration rates should be negligible. Thus, the heat evolution is likely  
303 to be dependent on clinker composition. The heat released during the first minutes is  
304 higher than for traditional OPC systems due to the higher content of rapidly soluble  
305 sulfates, and the fast dissolution of ye'elimite and other reactive phases when the  
306 particles come into contact with water [17]. Hargis *et al.* [60] reported that ye'elimite  
307 exhibits a relative low bulk modulus (~69 GPa), which can be attributed to its open  
308 aluminate framework as well as the high charges on the cation  $\text{Ca}^{2+}$  and anion  $\text{SO}_4^{2-}$  in  
309 intraframework sites. This increases its internal energy, and therefore its reactivity with  
310 water.

311 The absence of gypsum from the CSAB cements contributes to its high reactivity and  
312 accelerates the point of maximum heat release. The second peak, also described as the  
313 main hydration peak, corresponds to the reaction of ye'elimite ( $\text{C}_4\text{A}_3\bar{\text{S}}$ ), and also some  
314  $\text{C}_4\text{AF}$ , with calcium sulfate to form ettringite ( $\text{C}_6\text{A}\bar{\text{S}}_3\text{H}_{32}$ ) and amorphous aluminium  
315 hydroxide ( $\text{AH}_3$ ) (Eq. 1 and 2) [17].



316

317 Figure 3. Isothermal calorimetry curves for clinker pastes. A. CSAB-Ref, B. CSAB-  
318 RBX/AAS, and C. CSAB-AAS. In each plot, the left-hand vertical axis shows the rate  
319 of heat release, and the right-hand vertical axis shows the cumulative heat release.

320

321 The different crystal structures identified for the ye'elimite polymorphs in each of the  
322 clinkers synthesised may also contribute to the differences in their kinetic behaviour.  
323 Cuesta *et al.* (2014) [20] assessed the reactivity of the polymorphs of synthetic  
324 ye'elimite, where the orthorhombic ye'elimite reacts more slowly than the cubic  
325 ye'elimite. Such behaviour is aligned with the results reported here, as the CSAB-AAS

326 showed the highest heat release in the first 4 h due to its higher cubic ye'elinite content  
327 (Table 4); a higher cubic/orthorhombic ye'elinite ratio is observed when AAS is used  
328 in the raw meal mixes. On this basis, the lower reactivity of CSAB-Ref (mainly at early  
329 age) cannot be attributed solely to the presence of ternesite in this clinker. Ternesite has  
330 been also identified as a secondary phase in CSAB clinkers [13,14,31,34,62,63], where  
331 contradictory results regarding its hydration behaviour are reported. Ternesite is often  
332 considered to decrease the setting rate of CSAB, potentially acting as an inert phase  
333 with very low reactivity degree [64–67]. However, the aluminium released during  
334 ye'elinite hydration has a strong influence on ternesite reactivity, as the dissolution rate  
335 of ternesite is affected by the presence of soluble sulfate sources ( $\text{C}\bar{\text{S}}$  or  $\text{C}\bar{\text{S}}\text{H}_2$ ) and the  
336 availability of  $\text{Al}(\text{OH})_4^-$  within the pore solution [14,31,68].

337 The evolution of heat during hydration of CSAB-Ref shows a second heat release up to  
338 1.5 h, which is considerably delayed compared with the CSAB-Bx/AAS and CSAB-  
339 AAS clinkers, where this period only lasts around 25 min. Although the CSAB-Ref  
340 exhibited the lowest maximum heat release in the first two hours of reaction, its  
341 cumulative heat of hydration after 24 h was 172.3 J/g, which is higher by 48% and 11%  
342 than the corresponding data obtained for CSAB-Bx/AAs and CSAB-AAs, respectively  
343 (Figure 3B,C).

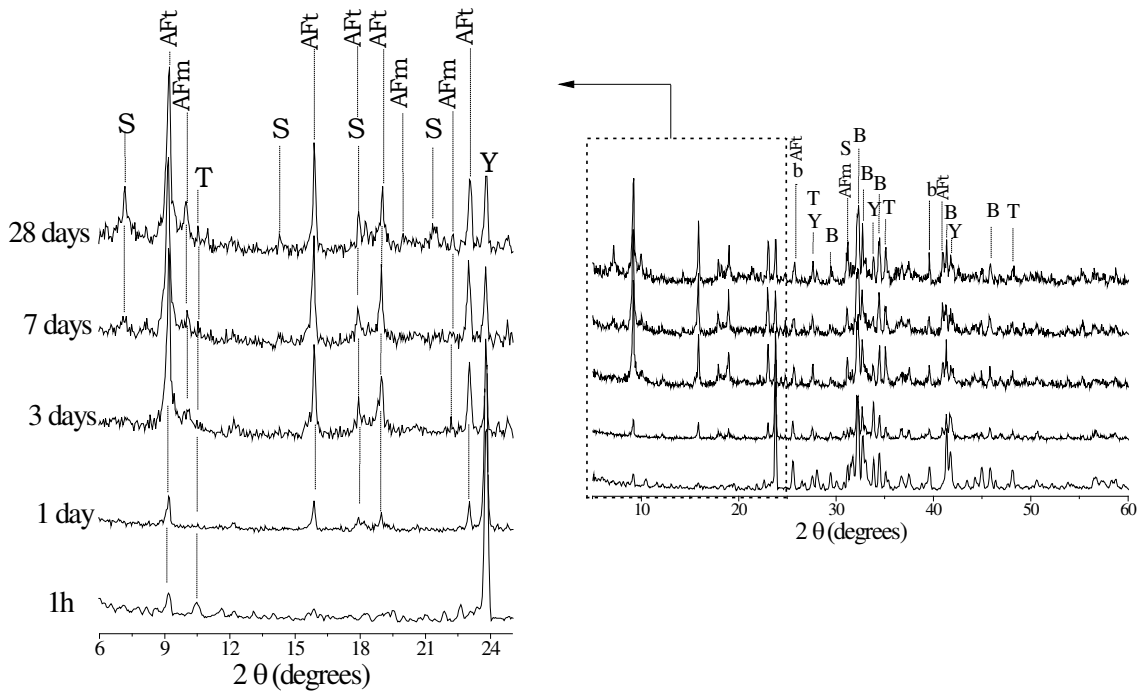
### 344 3.2.2. X-ray diffraction analysis of hydrated CSAB clinkers

345 Figure 4 shows the XRD pattern in a  $2\theta$  range between 6 and 25 degrees for the  
346 hydrated pastes up to 28 days of curing. As main crystalline hydration products in the  
347 CSAB pastes, ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ ;  $\text{C}_6\bar{\text{A}}\bar{\text{S}}_3\text{H}_{32}$ , PDF# 00-031-0251)  
348 and  $\text{SO}_4\text{-AFm}$  ( $\text{Ca}_4\text{Al}_2\text{SO}_{10}\cdot 12\text{H}_2\text{O}$ ; PDF# 00-045-0158) were identified. At 28 days,  
349 the consumption of ye'elinite, as well as the presence of belite and  $\text{AH}_3$  (which would

350 be present as an amorphous phase) lead to the crystallization of a strätlingite-type AFm  
351 phase ( $\text{Ca}_2\text{Al}_2\text{SiO}_7 \cdot 8\text{H}_2\text{O}$ ; PDF# 00-029-0285). Residual crystalline phases in non-  
352 hydrated CSAB clinker grains, such as ye'elimite, belite, and ternesite, were identified  
353 in the hydrated paste at all ages assessed. These results are in accordance with other  
354 reports where residual ye'elimite has been identified in hydrated pastes even after 360  
355 days of curing [69].

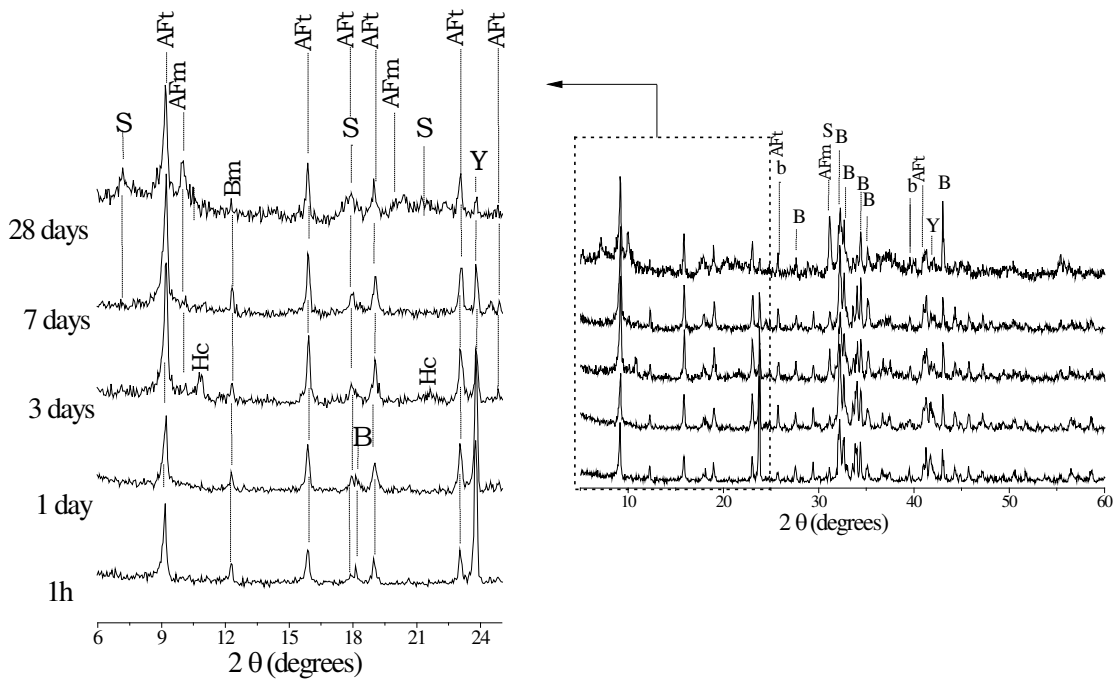
356 The higher degree of consumption of ye'elimite during the hydration of CSAB-AAS  
357 than the other samples tested is evident from the XRD analysis (more evident in the data  
358 for 1 day samples, and related to the content of cubic ye'elimite which has high  
359 reactivity). These results are in good agreement with the fast dissolution of sulfate  
360 phases and subsequent ettringite precipitation identified through the higher heat release  
361 during the first minutes (Figure 3A). According to Chen and Juenger [24], and Jawed  
362 and Skalny [70], the dissolved alkali concentration during hydration could also increase  
363 for the CSAB-ASS and CSAB-Bx/ASS clinkers due to the release of  $\text{Na}^+$  and  $\text{K}^+$  from  
364 the reactive anhydrous phases, which increase the dissolution rate of aluminate phases  
365 (in particular  $\text{C}_4\text{A}_3\bar{\text{S}}$ ) and the subsequent formation of ettringite and  $\text{AH}_3$  phases.

A

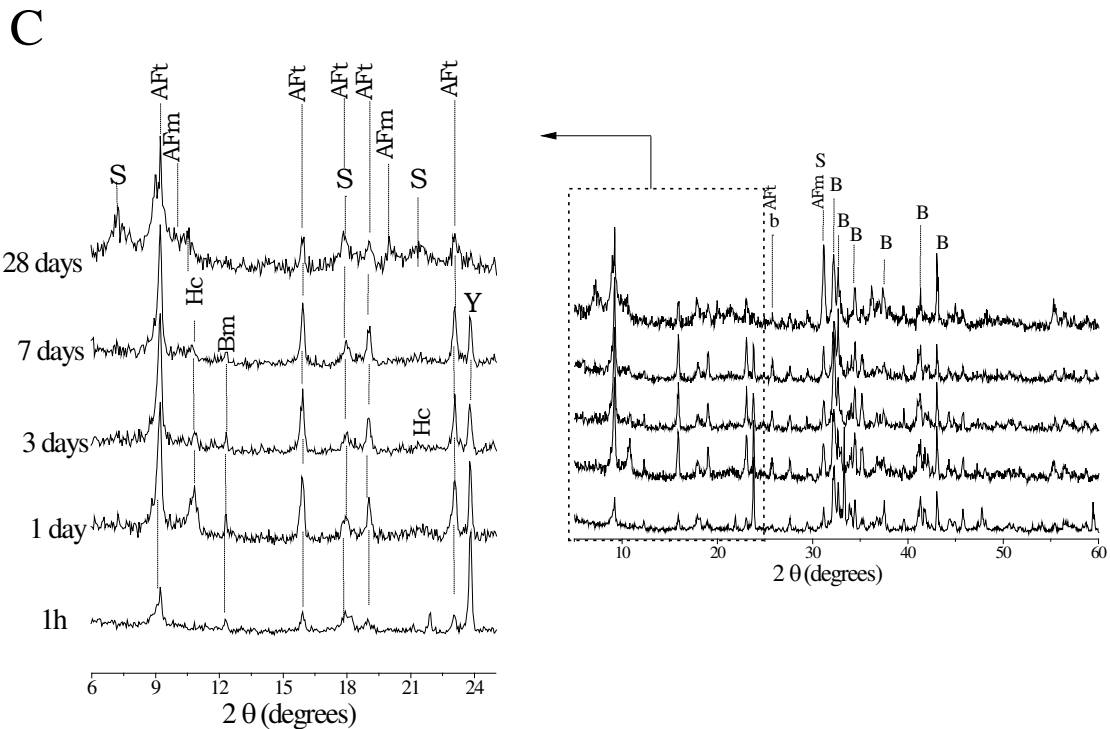


366

B



367



368

369 Y: ye'elimite; B: belite; T: ternesite; Bm: brownmillerite; AFt: ettringite; AFm: calcium monosulfoaluminate hydrate;

370

Hc: calcium hemicarboaluminate hydrate; S: strätlingite.

371 Figure 4. X-ray diffractograms of hydrated pastes up to 28 days of curing. A. CSAB-

372 Ref; B. CSAB-Bx/AAS; and C. CSAB-AAS.

373 After ettringite formation is close to complete – the corresponding XRD peaks exhibit

374 the highest intensity after 3 days of curing – AFm products start to form. Contrary to

375 other reports [14,16,18,19], portlandite (CH), hydrogarnet and calcium silicate hydrate

376 were not identified as hydrate products here. The presence of belite, which acts as a

377 silica source, as well as the  $C_4A_3\bar{S}$  and/or  $AH_3$  as aluminium sources, can lead to the

378 formation of strätlingite [71], for example according to the equation  $C_2S + AH_3 + 5H \rightarrow$

379  $C_2ASH_8$  [17]. As the hydration proceeds, calcium hemicarboaluminate hydrate

380  $(Ca_4Al_2(OH)_{12}(OH)(CO_3)_{0.5} \cdot nH_2O; (CO_3,OH)\text{-AFm}$ , PDF # 00-036-0129) is formed

381 from CSAB-Bx/AAS and CSAB-AAS clinkers after 3 days and 1 day of curing,

382 respectively, but then was not identified at later ages. This suggests that the samples

383 were taking up  $CO_2$  from the ambient atmosphere, taking into account the slow kinetics

384 of dissolution of calcium carbonate [72], as well as the higher thermodynamic stability  
385 of (CO<sub>3</sub>,OH)-AFm phases compared to monosulfate [73].

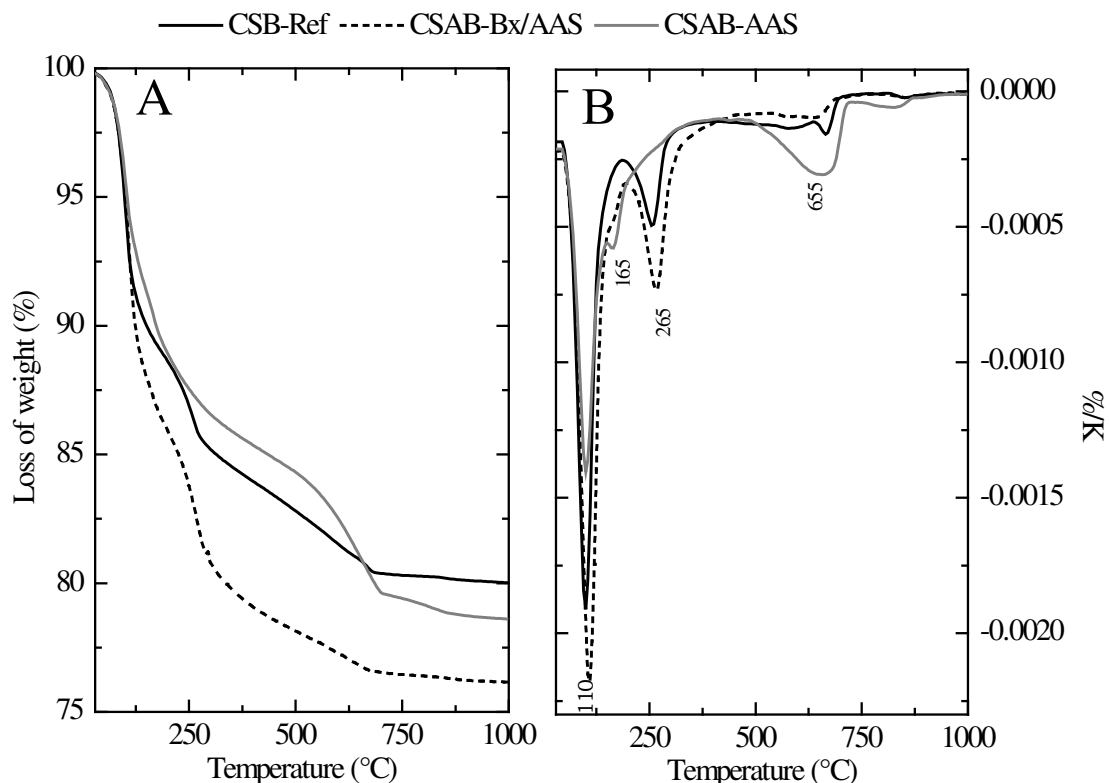
386 The low reactivity of belite contributes to the low silica availability in these binders  
387 during the early stages of reaction, and strätlingite is only detected after 7 days of  
388 curing. At later age, further formation of strätlingite is identified. This phase can exhibit  
389 low crystallinity, small crystal size and/or internal disorder during its crystallisation as  
390 evidenced by the broad XRD peaks observed (Figure 4), particularly for CSAB-AAS  
391 [74]. This higher degree of disorder can be attributed to the high affinity of strätlingite  
392 for alkali metal cations, which reduce the regularity of its structure, and so this is  
393 observed mainly for those clinkers with high contents of sodium and potassium [17].  
394 Santacruz *et al* [75], reported that the microstructure of strätlingite can be also affected  
395 by dehydration when the sample is dried for characterisation. This slight drying damage  
396 changes the interlayer spacing, meaning that the main (003) peak can be broadened and  
397 shifted.

398 According to Bullerjahn *et al.* [14], the presence of ternesite reduces C<sub>2</sub>S reactivity  
399 during the hydration of a belite calcium sulfoaluminate ferrite clinker. This is in good  
400 agreement with the results presented here, where the CSAB-Ref, which contained 16%  
401 ternesite, also showed lower formation of strätlingite than the other clinkers after 28  
402 days of curing.

### 403 3.2.3. Thermogravimetry

404 The thermogravimetric analysis (Figure 5) shows a higher reactivity for C $\bar{S}$ AB-Bx/AAS  
405 than the other clinkers, as seen by the higher content of hydrated products formed.  
406 C $\bar{S}$ AB-Ref exhibited a total mass loss of ~20%, which is 19% less than that of CSAB-

407 Bx/AAS. The differential thermogravimetry (DTG) curves show a pronounced peak  
408 located at 110 °C corresponding to the loss of hydrate water from ettringite [76]. A  
409 second peak is identified at ~260 °C, associated with amorphous Al(OH)<sub>3</sub>. The very  
410 similar position of this peak between CSAB-Bx/AAS and CSAB-Ref elucidates the  
411 similar environments of the bound water in these samples. According to Kuzel [77], the  
412 peak at 160 °C for the CSAB-Bx/AAS paste can be attributed to strätlingite, which  
413 exhibits three endothermic peaks, a minor peak at ~120 °C and main peaks at 165 and  
414 220 °C. It is not possible to separately quantify the amount of ettringites and AFm-type  
415 phases, including strätlingite, from TGA as their temperatures of decomposition (30-  
416 180 °C) overlap [78]. The set of peaks located between 650 and 710 °C are attributed to  
417 decomposition of carbonates formed due to superficial carbonation of the samples.

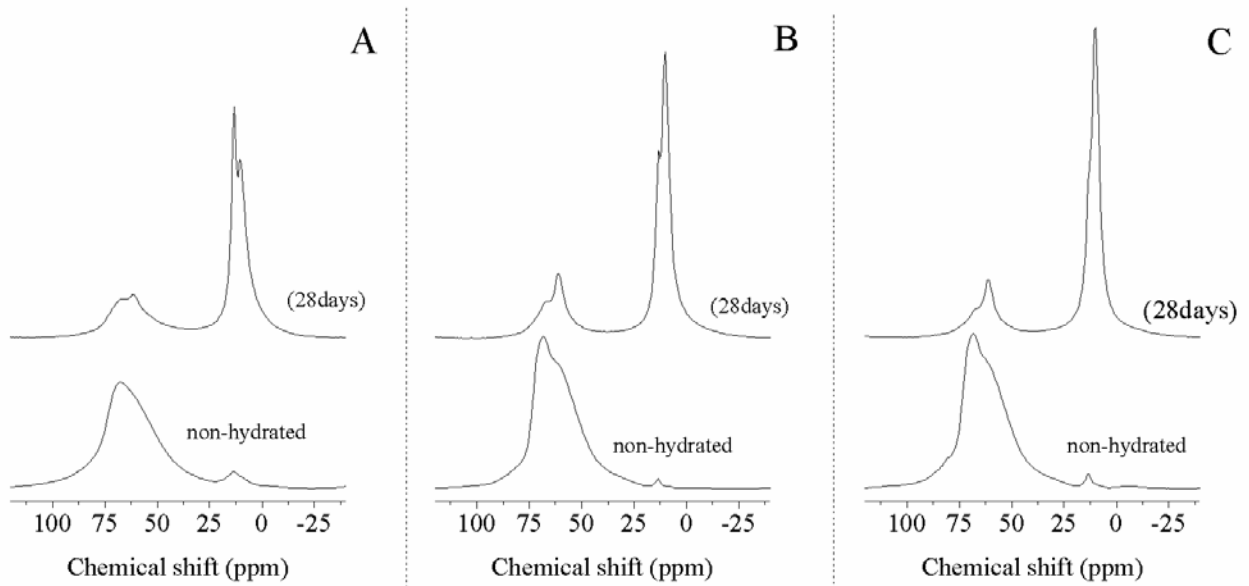


418  
419 Figure 5. Thermogravimetric analysis for CSAB clinker hydration products after 28  
420 days of curing.  
421

422 3.2.4. *Solid-state NMR spectroscopy*

423 The  $^{27}\text{Al}$  MAS NMR spectra for anhydrous clinkers and the pastes after 28 days of  
424 curing are shown in Figure 6. The clinkers show a wide band with two signals located at  
425 50 – 80 ppm, corresponding to structurally distinct tetrahedrally coordinated Al sites.  
426 These signals can be attributed mainly to the ye'elimite, and any Al substituting for Si  
427 in alite or belite will also contribute to the downfield region of this resonance [79]. The  
428 Al present in the aluminoferrite phases identified by XRD does not contribute  
429 considerably to the  $^{27}\text{Al}$  MAS NMR spectra due to the high concentration of  $\text{Fe}^{3+}$   
430 present either in paramagnetic or antiferromagnetic form in this phase [80]. The effect  
431 of  $\text{Fe}^{3+}$  on the  $^{27}\text{Al}$  MAS NMR spectra of CSAB clinkers assessed here is not yet well  
432 identified, especially due to the wide range of Al/Fe ratios present in the ferrite phases.  
433 The signal of  $\text{Al}^{\text{IV}}$  for CSAB-Ref clinker is broad with a maximum located at ~68 ppm,  
434 while the clinkers produced with alternative  $\text{Al}_2\text{O}_3$  sources (CSAB-Bx/AAS and CSAB-  
435 AAS) show a more intense peak, which also has a shoulder located at ~60 ppm. The  
436 weak signal located at ~13 ppm for the clinkers can be attributed to the  $\text{Al}^{\text{VI}}$ , which is  
437 either present as a guest ion in the belite phase [79], or the partial pre-hydration of the  
438 ye'elimite through contact with atmospheric moisture.

439



440

441 Figure 6.  $^{27}\text{Al}$  MAS NMR spectra of anhydrous clinkers and CSAB pastes after 28 days  
442 of curing. A. CSAB-Ref; B. CSAB-Bx/AAS and C. CSAB-AAS.

443

444 The dissolution and subsequent hydration of reactive phases modify the molecular  
445 environment, and a more intense peak between 0 and 20 ppm is identified in the  
446 hydrated paste samples. The hydration reaction considerably reduces the signal  
447 attributed to  $\text{Al}^{\text{IV}}$ ; instead, a narrower and very much intense  $\text{Al}^{\text{VI}}$  peak is obtained. This  
448 is associated with the ye'elimite dissolution and subsequent formation of ettringite  
449 whose octahedrally-coordinated Al is identified at ~13 ppm. The partially overlapping  
450 signal identified at ~10 ppm can be assigned to the AFm-type phases including  
451 strätlingite [81].

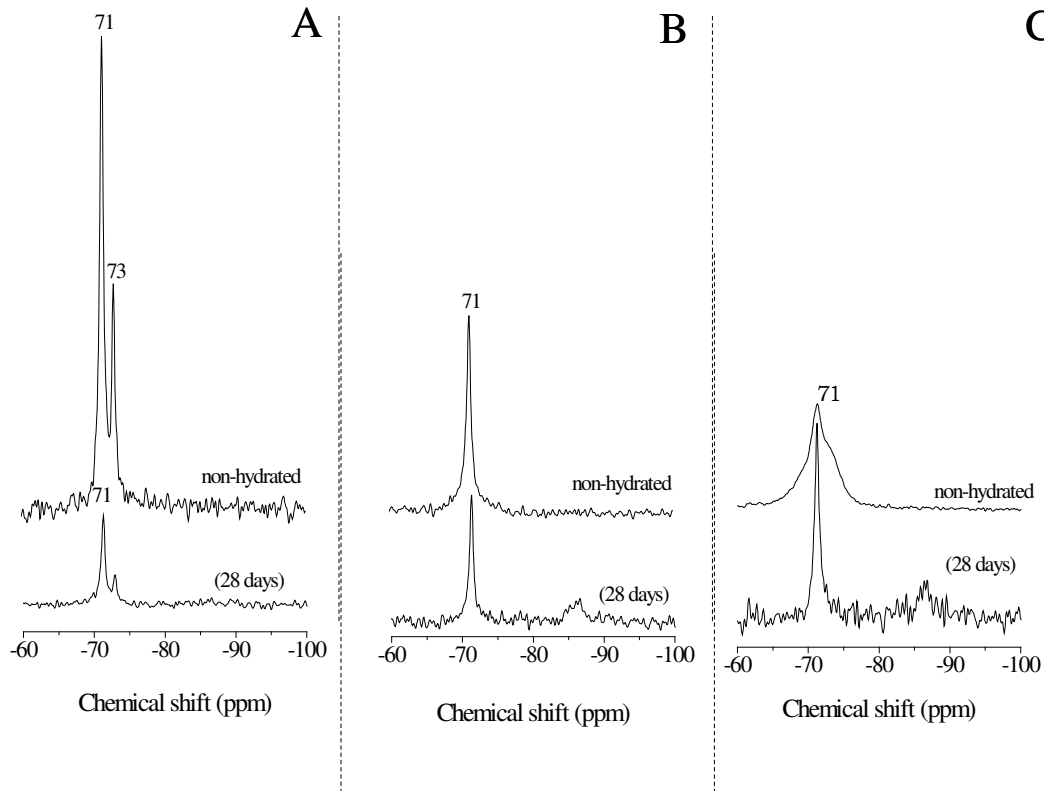
452 In the hydrated paste of CSAB-Bx/AAS, the peak attributed to the ettringite (~13 ppm)  
453 showed a lower intensity when compared to the AFm-type phases (~10 ppm), although  
454 these peaks do partially overlap. The hydration products of the clinkers produced with  
455 partial or total substitution of bauxite (CSAB-Bx/AAS and CSAB-AAS) showed more  
456 formation of AFm-type phases. This effect is more pronounced for samples produced

457 using a higher content of AAS. These results are consistent with the XRD data where a  
458 reduction in the ettringite content can also be identified after 28 days of curing (Figure  
459 4C), as this is partially converted to monosulfate as the reaction progresses. The absence  
460 of a defined signal at ~4 ppm suggests the presence of at most a low concentration of  
461  $\text{AlH}_3$  at 28 days, although this environment might be overlapped by the octahedrally Al  
462 coordinated sites of the AFm and AFt phases [82,83]. The aluminium in strätlingite is  
463 present in both IV-fold and VI-coordinations, but the presence of alkalis within the  
464 structure, mainly for the clinkers produced with AAS, reduces the  $\text{Al}^{\text{IV}}/\text{Al}^{\text{VI}}$  ratio [84].  
465 The signal at 61 ppm for the pastes after 28 days of curing corresponds to the  $\text{Al}^{\text{IV}}$   
466 environment within strätlingite, while its  $\text{Al}^{\text{VI}}$  peak overlaps with those of the other  
467 AFm phases present [84]. Therefore, the higher intensity of the peak located at ~10 ppm  
468 for the hydrated CSAB-AAS clinkers is attributed to the higher degree of formation of  
469 AFm phases including strätlingite, consistent with the diffractograms shown in Figure 4.  
470 The presence of residual unreacted ye'elimite even after 28 days of curing is indicated  
471 by the lower but non-zero intensity of the main broad peak attributed to  $\text{Al}^{\text{IV}}$  in this  
472 phase. Differences in this peak between samples indicate a greater extent of hydration  
473 for the CSAB-Bx/AAS and CSAB-AAS clinkers compared to CSAB-Ref.

474 The  $^{29}\text{Si}$  MAS NMR spectra for the anhydrous clinkers and their corresponding pastes  
475 at 28 days of curing are shown in Figure 7. The spectra for the anhydrous CSAB-Ref  
476 and CSAB-Bx/AAS exhibited a narrow resonance at -71 ppm relative to TMS ( $\text{Q}^0$  sites)  
477 corresponding to the  $\text{C}_2\text{S}$  phase (Figure 7A and B), which is consistent with the XRD  
478 results. The CSAB-AAS clinker exhibited a broader peak with a maximum at -71 ppm  
479 along with a shoulder located at ~-74 ppm (Figure 7C). These features can be attributed  
480 to the tricalcium silicate as identified by XRD in Figure 1. This structure contains nine  
481 non-equivalent silicon sites, with overlapping resonances in a spectral range between -

482 66 and -77 ppm [85], although the presence of paramagnetic ions and different degrees  
483 of guest-ion incorporation (such as  $Mg^{2+}$ ,  $S^{6+}$ ,  $Al^{3+}$ ) modify the distribution of silicon-  
484 oxygen distances and broaden the  $^{29}Si$  MAS NMR spectra [86]. The peak at -73 ppm in  
485 CSAB-Ref (Figure 7A) can be attributed to the presence of ternesite [87].

486 The  $^{29}Si$  NMR spectra for every paste exhibited residual  $C_2S$  from the clinker  
487 (resonance at -71 ppm), which is also consistent with the presence of belite in the XRD  
488 results. The highest consumption of  $C_2S$  is observed for CSAB-Bx/AAS followed by  
489 CSAB-AAS. A significant reduction of the characteristic peak attributed to ternesite  
490 corroborates its dissolution during hydration. The low content of alite in CSAB-  
491 Bx/AAS and CSAB-AAS could lead to the formation of a C-S-H-type phase with short-  
492 range order, not identifiable by XRD. The silicate chains in this type of phase show  $^{29}Si$   
493 chemical shifts of -80 to -90 ppm, mainly being present as  $Q^1$ ,  $Q^2$  and  $Q^2(1Al)$  units.  
494 Therefore, the weak broad signal around -87 ppm in the samples can be attributed to the  
495 presence of both C-S-H and strätlingite [84], and there is a superposition of unresolved  
496 signals from these Si environments. The high content of vacancies and/or substitutions  
497 in the strätlingite structure tend to decrease the Si connectivity and a more disordered  
498 structure can be obtained, which is coherent with the XRD results (Figure 4) showing a  
499 broad main strätlingite peak consistent with structural disorder.



500

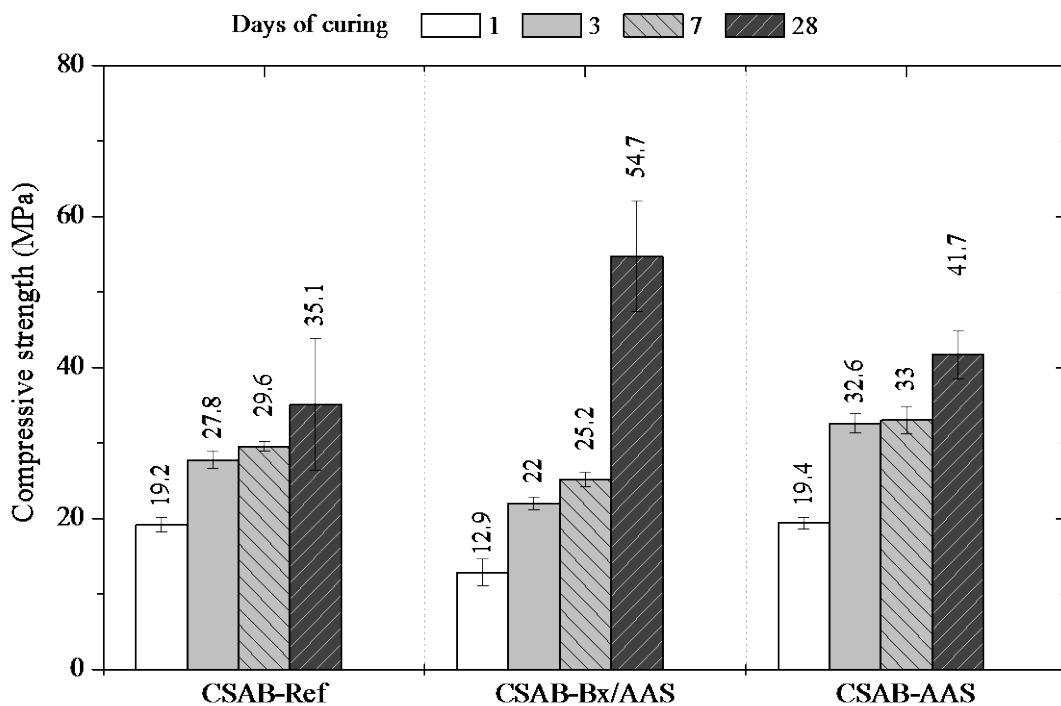
501 Figure 7.  $^{29}\text{Si}$  MAS NMR spectra of anhydrous clinkers and CSAB pastes after 28 days  
502 of curing. A. CSAB-Ref; B. CSAB-Bx/AAS and C. CSAB-AAS. Note that the vertical  
503 scale for the 28-day cured material in C is exaggerated by a factor of  $\sim 2$  to emphasise  
504 the formation of the new hydrate product peak.

505

### 506 3.2.5. Compressive strength

507 The results obtained for the mechanical performance of the hydrated pastes of each  
508 clinker at different ages of curing are shown in Figure 8. The compressive strengths  
509 achieved by the CSAB clinkers produced with the alternative alumina source show a  
510 marked difference, despite their similar chemical compositions (Table 3). At early age,  
511 CSAB-Bx/AAS shows a compressive strength up to  $\sim 32\%$  lower than those of CSAB-  
512 AAS and CSAB-Ref. This higher mechanical performance for CSAB-Ref and CSAB-  
513 AAS at early age can be attributed to a greater initial extent of hydration, also shown by

514 the higher heat release during the first 24 hours of hydration. The clinkers produced  
515 with AAS (CSAB-Bx/AAS and CSAB-AAS) increase their compressive strength by  
516 ~70% from 1 day to 7 days of curing, leading to strength performance after 28 days  
517 which is considerably higher than that of CSAB-Ref. The growth in compressive  
518 strength is also higher with longer-term curing of CSAB-Bx/AAS, which can be  
519 attributed to the presence of a higher content of C<sub>2</sub>S (see Table 3) contributing to long-  
520 term compressive strength development through the formation of strätlingite [1,16].



521

522 Figure 8. Compressive strength of CSAB clinker pastes up to 28 days of curing.

523

#### 524 4. Conclusions

525 This study has demonstrated the potential valorisation of an aluminium anodising  
526 sludge – a waste from the aluminium processing industry – as aluminium source in the  
527 production of calcium sulfoaluminate-belite (CSAB) clinkers. Ye’elimitite and belite

528 were the main phases formed in clinkerisation, with anhydrite and aluminoferrite-type  
529 phases identified as secondary phases. Ternesite was also identified in the reference  
530 CSAB clinker produced with mineral reagents, but not when the anodising sludge was  
531 used. The use of traditional raw materials (such as bauxite and limestone), as well as an  
532 alternative aluminium source has a strong effect on the clinkerisation process as a  
533 consequence of the high content of foreign ions, such as Na, K and Mg. As the content  
534 of aluminium anodising sludge increases, a higher content of alite is formed. The  
535 content of both cubic and orthorhombic ye'elinite is also influenced by the inclusion of  
536 aluminium anodising sludge. The ratio between these different polymorphs identified in  
537 each of the clinkers synthesised, and the presence of ternesite, appear to play an  
538 important role in determining the kinetics of hydration.

539 Ettringite and calcium monosulfoaluminate hydrate were identified as the main  
540 crystalline hydration products in all pastes studied. The presence of belite along with the  
541 remaining ye'elinite and/or newly formed amorphous aluminium hydroxide leads to the  
542 formation of strätlingite at later ages. These hydrated products, derived from the slightly  
543 higher content of belite in the clinkers based on aluminium anodising sludge,  
544 contributed to higher compressive strength at 28 days of curing when compared with the  
545 reference CSAB clinker.

546

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