



This is a repository copy of *Slag-Based Cements That Resist Damage Induced by Carbon Dioxide*.

White Rose Research Online URL for this paper:  
<http://eprints.whiterose.ac.uk/131401/>

Version: Accepted Version

---

**Article:**

Ke, X. [orcid.org/0000-0002-1239-6861](https://orcid.org/0000-0002-1239-6861), Criado, M. [orcid.org/0000-0002-1027-6233](https://orcid.org/0000-0002-1027-6233), Provis, J.L. [orcid.org/0000-0003-3372-8922](https://orcid.org/0000-0003-3372-8922) et al. (1 more author) (2018) Slag-Based Cements That Resist Damage Induced by Carbon Dioxide. *ACS Sustainable Chemistry and Engineering*, 6 (4). pp. 5067-5075. ISSN 2168-0485

<https://doi.org/10.1021/acssuschemeng.7b04730>

---

**Reuse**

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.



[eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk)  
<https://eprints.whiterose.ac.uk/>

## A slag-based cement that resists damage induced by carbon dioxide

Xinyuan Ke, Maria Criado, John L. Provis, and Susan A. Bernal

*ACS Sustainable Chem. Eng.*, **Just Accepted Manuscript** • DOI: 10.1021/  
accsuschemeng.7b04730 • Publication Date (Web): 01 Mar 2018

Downloaded from <http://pubs.acs.org> on March 3, 2018

### Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.



# A slag-based cement that resists damage induced by carbon dioxide

Xinyuan Ke, Maria Criado, John L. Provis\*, Susan A. Bernal\*

Department of Materials Science and Engineering, Sir Robert Hadfield Building, The University of Sheffield, Mappin St, Sheffield S1 3JD, United Kingdom

\* To whom correspondence should be addressed. Email: [s.bernal@sheffield.ac.uk](mailto:s.bernal@sheffield.ac.uk); [j.provis@sheffield.ac.uk](mailto:j.provis@sheffield.ac.uk); phone +44 114 222 5490; fax +44 114 222 5493

## Abstract

The use of sodium carbonate as an activator to prepare alkali-activated cements from blast furnace slag and calcined hydrotalcite offers many attractive performance and environmental benefits. However, the understanding of the long-term performance of these cements is limited. In this study, the resistance of sodium carbonate-activated slag cements to carbonation attack was determined under natural (0.04%) and elevated (1.0%) CO<sub>2</sub> concentrations. Two calcium carbonate polymorphs, calcite and vaterite, were formed as carbonation products at a longer time of CO<sub>2</sub> exposure. A cross-linked alkali aluminosilicate gel, and a Ca-deficient calcium (alumino)silicate hydrate gel were identified to form by decalcification of the main binding phases initially present in these cements. However, despite these carbonation-induced mineralogical changes, the mechanical strength after carbonation was comparable to that of non-carbonated specimens, which is contrary to previous observations of strength loss due to carbonation of slag-rich cements. The high carbonation resistance of sodium carbonate-activated slag cement indicates these materials have the potential to resist attack by atmospheric CO<sub>2</sub> in service with sustained mechanical performance.

**Keywords:** Alkali-activated cements, carbonation, calcium carbonate, durability, layered double hydroxides.

## 30 Introduction

31 The cement industry is facing the challenge of reducing its environmental footprint while  
32 dealing with a continuously increasing demand for this essential material. This has motivated  
33 the development of non-Portland cements, including alkali-activated cements (AACs), which  
34 are prepared using the powders that are normally blended with Portland cement (PC) as  
35 supplementary cementitious materials (e.g. blast furnace slags, fly ashes, calcined clays, and  
36 others) together with an alkali activator which enables them to generate cementing character  
37 and high mechanical performance without the addition of Portland clinker<sup>1-2</sup>. In many  
38 aspects AACs develop performance which is comparable to that of blended Portland-based  
39 cements<sup>2-3</sup>.

41 The selection of the alkali source used as the activator strongly influences the  
42 microstructural features and the physico-mechanical performance of an AAC<sup>4-6</sup>, as well as  
43 the environmental impacts associated with its production<sup>7-9</sup>. The most commonly used  
44 activators include sodium hydroxide and sodium silicate. A recent life cycle analysis of  
45 AACs revealed that although these cements have much lower global warming potentials than  
46 PC, the use of sodium hydroxide and/or sodium silicate as activators brings a higher  
47 environmental impact in aspects including human toxicity, fresh water and marine ecotoxicity  
48<sup>9</sup>. The industrial production of sodium silicate is also an energy intensive process, and the  
49 commonly used furnace process requires reacting sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sand ( $\text{SiO}_2$ )  
50 at 1100-1200 °C<sup>10</sup>. To replace sodium silicate with sodium carbonate, as an alternative  
51 alkali-activator, has the potential to greatly reduce the environmental impact of alkali-  
52 activated cements, especially in regions where there are abundant geological resources of  
53 sodium carbonate that can be mined from trona deposits<sup>11</sup>. The sodium carbonate produced  
54 from natural deposits is now around a quarter of the global production,<sup>12</sup> and this process  
55 leads to significantly lower greenhouse gas emissions than the industrial synthesis of sodium  
56 carbonate by the Solvay process<sup>13</sup>.

58 It is well known that alkali-activation of blast furnace slag to form cements is achievable  
59 using mild alkaline solutions based on sodium carbonate<sup>2, 4, 14-17</sup>. However, earlier attempts  
60 using sodium carbonate as the sole activator were barely satisfactory in terms of use in  
61 modern engineering and construction practice, as prolonged setting times (up to 1-5 days at

1  
2  
3 62 ambient temperature) were observed, followed by slow development of strength <sup>3, 18-19</sup>.  
4 63 Recent studies have elucidated that the consumption of carbonate anions supplied by the  
5 64 activator dominates the early kinetics of reaction of these cements <sup>17</sup>. In particular, the  
6 65 formation of a layered double hydroxide hydrotalcite-like phase ( $[\text{Mg}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}[\text{OH},\text{CO}_3]_{x/m}\cdot n\text{H}_2\text{O}$ ,  $0.20 < x < 0.33$ ,  $m$ : charge of anion and  $n$ : hydration number),  
7 66 in parallel with other carbonate-containing phases, plays a key role in chemically binding the  
8 67 carbonate present in the pore solution <sup>20</sup> and can be tailored to promote fast hardening.  
9 68 Incorporation of a small fraction of a calcined mineral addition designed to favor the  
10 69 formation of this phase (specifically, a calcined layered double hydroxide, CLDH) into these  
11 70 cements can greatly enhance this effect. The addition of this CLDH also promotes good  
12 71 mechanical performance, and reduces chloride permeability compared with sodium silicate-  
13 72 activated AAC, or with Portland cement <sup>20-21</sup>.  
14 73  
15 74

16 75 The carbonation of cement hydrate products is one of the main degradation mechanisms of  
17 76 cements and concretes, and involves a chemical reaction between the alkaline binder and the  
18 77  $\text{CO}_2$  present in the atmosphere. Thus, significant attention is paid to this process when  
19 78 assessing the durability performance of concrete structures in many exposure conditions, as it  
20 79 can induce a reduction of the pH within the concrete and consequently increase the  
21 80 probability of corrosion of steel reinforcement <sup>22-24</sup>. However, the carbonation of cements in  
22 81 service has also been identified as a large potential carbon sink <sup>22, 25</sup>, before reaching the point  
23 82 that the carbonation-induced degradation would jeopardize the safety performance of the  
24 83 structure. In Portland cement, the presence of portlandite ( $\text{Ca}(\text{OH})_2$ ) provides a buffer phase,  
25 84 consuming atmospheric  $\text{CO}_2$  as it is converted to calcium carbonate. This delays the  
26 85 decalcification process of the main strength-giving phase, a calcium silicate hydrate <sup>26</sup>.  
27 86 However, in AACs, the absence of portlandite and the high alkalinity of the pore solution  
28 87 have made carbonation one of the main durability-related concerns <sup>27-28</sup>. For the specific case  
29 88 of sodium carbonate-activated slag cement, the information available from the literature  
30 89 regarding its resistance to carbonation is very limited. However, it has been observed that  
31 90 after exposure to atmosphere conditions for over 35 years, sodium carbonate-activated slag  
32 91 concrete presented an increased strength <sup>29</sup>, suggesting that the carbonation process taking  
33 92 place in these cement most likely differs from that in sodium silicate-activated slag cements,  
34 93 which tends to lose strength as a result of carbonation <sup>30-31</sup>. Hence, the development of a new  
35 94 fundamental understanding of the structural changes induced by carbonation of sodium

1  
2  
3 95 carbonate-activated slag cement is crucial, not only for assessment of its durability  
4 96 performance, but also for evaluation of its whole-service-life carbon footprint.  
5  
6  
7 97

8 98 Therefore, in this study, the structural stability of sodium carbonate-activated slag cements  
9 99 upon exposure to natural and high CO<sub>2</sub> concentrations was determined, as well as the effects  
10 100 of its chemical modification via the addition of a calcined layered double hydroxide, as a  
11 101 potential CO<sub>2</sub> binding agent.  
12  
13  
14  
15  
16 102

## 17 103 **Experimental Program**

### 18 104 **Materials**

19  
20  
21 105 A commercial ground granulated blast furnace slag was used in this study, a glassy  
22 106 material mainly consisting of CaO (41.3 wt.%), SiO<sub>2</sub> (36.0 wt.%), Al<sub>2</sub>O<sub>3</sub> (11.3 wt.%), and  
23 107 MgO (6.5 wt.%). This slag had a Blaine fineness of  $5056 \pm 22$  cm<sup>2</sup>/g (average value of four  
24 108 measurements), and an average particle size  $d_{50}$  of  $11.2 \pm 0.1$  μm (determined using laser  
25 109 diffraction).  
26  
27  
28  
29  
30  
31 110

32 111 The activator was prepared by pre-dissolving commercial sodium carbonate powder  
33 112 (Sigma Aldrich, Na<sub>2</sub>CO<sub>3</sub> ≥ 99.5%) into distilled water. A calcined layered double hydroxide  
34 113 (CLDH) was produced by thermally treating synthetic hydrotalcite (Sigma Aldrich) at 500°C,  
35 114 following the procedure described in a previous study<sup>20</sup>, where detailed characterization of  
36 115 the synthetic hydrotalcite, before and after treatment, was reported.  
37  
38  
39  
40  
41 116

### 42 117 **Sample preparation**

43  
44  
45 118 Sodium carbonate-activated slag pastes were produced with an activator dose of 8 g  
46 119 Na<sub>2</sub>CO<sub>3</sub> per 100 g slag, and a water/(slag+Na<sub>2</sub>CO<sub>3</sub>) mass ratio of 0.40. To some of the pastes,  
47 120 5 wt.% CLDH (by mass of anhydrous slag) was also added. Pastes were mixed using an  
48 121 overhead mixer with a high-shear blade, cast in centrifuge tubes, then sealed and stored at  
49 122 room temperature ( $20 \pm 3$  °C) until testing. Sodium carbonate-activated slag mortars were  
50 123 also prepared with a sand to slag mass ratio of 3:1, where BS EN 196-1 standard sand<sup>32</sup> was  
51 124 used, and cured under the same conditions as the pastes.  
52  
53  
54  
55  
56  
57  
58  
59  
60

125

**126 Test methods**

127 Slag paste samples that had been cured for 28 and 180 days were crushed and sieved to a  
128 particle size of between 100  $\mu\text{m}$  and 250  $\mu\text{m}$ , exposed to atmospheric carbonation ( $\sim 0.04\%$   
129  $\text{CO}_2$ , described as *naturally carbonated*), and elevated carbonation condition ( $1.0 \pm 0.2\%$   
130  $\text{CO}_2$ , described as *accelerated carbonated*). Under both carbonation conditions, the  
131 temperature and relative humidity was controlled at  $20 \pm 2$   $^\circ\text{C}$  and  $65 \pm 5\%$ , respectively. The  
132 accelerated carbonation conditions were selected based on a previous study<sup>28</sup> where it was  
133 demonstrated that alkali-activated samples carbonated under these conditions develop  
134 comparable carbonation reaction products to those forming after several years of atmospheric  
135 exposure. Pastes exposed to both  $\text{CO}_2$  conditions for up to 14 days were analyzed. Reference  
136 samples sealed in centrifuge tubes and kept under the same laboratory conditions ( $20 \pm 2$   $^\circ\text{C}$ ,  
137 described as *non-carbonated*) were analyzed at similar times to those used for carbonation, to  
138 account for the structural evolution taking place in these cements as they continued to mature  
139 during the period of  $\text{CO}_2$  exposure. Specimens were analyzed through:

140

- 141 • X-ray diffraction (XRD), using a Bruker D2 Phaser instrument with  $\text{Cu-K}\alpha$  radiation and a  
142 nickel filter. The tests were conducted with a step size of  $0.02^\circ$  and a counting time of 1  
143 s/step, from  $5^\circ$  to  $55^\circ 2\theta$ .
- 144 • Thermogravimetry-mass spectroscopy (TG-MS), in a Perkin Elmer TGA 4000 instrument  
145 coupled with a Hiden mass spectrometer. In each case, 30 mg of sample was tested from  
146  $30^\circ\text{C}$  to  $1000^\circ\text{C}$  at a heating rate of  $3^\circ\text{C}/\text{min}$ , under nitrogen flowing at 40 mL/min.
- 147 • Solid-state  $^{29}\text{Si}$  MAS NMR spectra were collected at 79.4 MHz on a Varian VNMRS 400  
148 (9.4 T) spectrometer, using a probe for 6.0 mm outer diameter zirconia rotors, and a  
149 spinning speed of 6 kHz. The  $^{29}\text{Si}$  MAS NMR spectra were collected with a  $90^\circ$  pulse  
150 duration of 4.6  $\mu\text{s}$ , a recycle delay of 5 s, and between 6000 and 17000 repetitions. The  
151 solid state  $^{27}\text{Al}$  MAS NMR spectra were acquired on the same spectrometer at 104.20  
152 MHz, using a probe for 4 mm outer diameter zirconia rotors, a spinning speed of 14 kHz  
153 with a pulse duration of 1  $\mu\text{s}$  (approximately  $25^\circ$ ), a recycle delay of 0.2 s, and a minimum  
154 of 7000 repetitions.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  chemical shifts are referenced to external samples of neat  
155 tetramethylsilane (TMS) and a 1.0 M aqueous solution of  $\text{Al}(\text{NO}_3)_3$ , respectively.

1  
2  
3 156 Mortar cubes with dimensions of 50×50 mm were used for testing compressive strength,  
4 157 which was determined using an automatic testing machine (Controls Automax5) with a  
5  
6 158 loading speed of 0.25 MPa/s. Triplicate samples were measured per curing condition at each  
7  
8 159 time point. The carbonation penetration depth after exposure of mortar cubes to natural and  
9  
10 160 accelerated carbonation was also determined, using a spray of 1 wt.% phenolphthalein  
11 161 indicator solution (dissolving 1.0 g of phenolphthalein in 50 mL of ethanol and then adding  
12 162 50 mL of water) onto a freshly split surface as an indicator.  
13  
14  
15 163

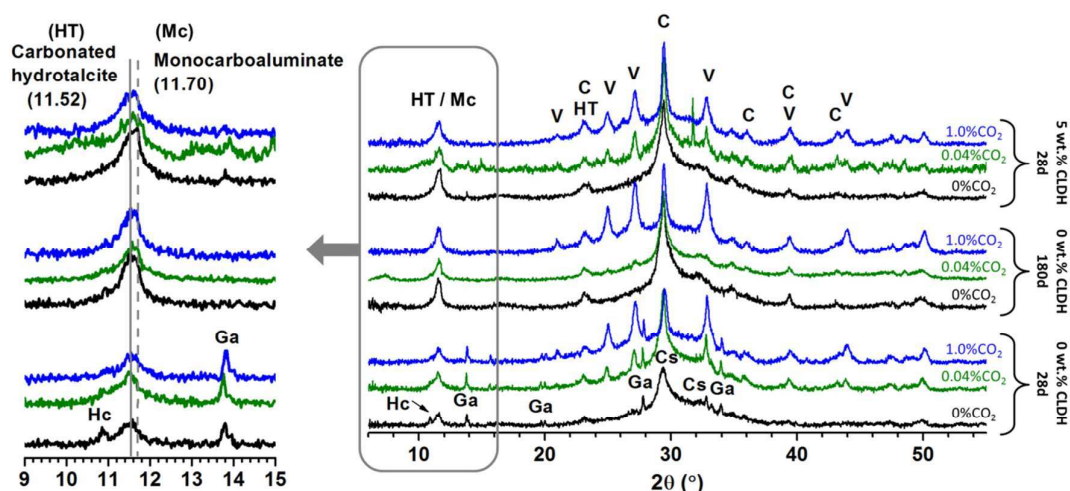
## 164 **Results and discussion**

### 165 **Formation of CaCO<sub>3</sub> polymorphs**

166 In accordance with previous evaluation of the phase evolution of sodium carbonate-  
167 activated slag cement<sup>20</sup>, the main reaction products identified by XRD analysis of the three  
168 non-carbonated samples assessed (0 wt.% CLDH after 28 and 180 days and 5 wt.% CLDH  
169 after 28 days, Figure 1) were semi-crystalline (Al, Na)-substituted calcium silicate hydrate  
170 (C-(N)-A-S-H) type gel (crystal structure close to PDF #00-019-0052), and layered double  
171 hydroxide phases including both hydrotalcite-structured and AFm-structured (hydrocalumite-  
172 like) phases. Specifically, the AFm phases identified by XRD were hemicarboaluminate  
173 (PDF #00-036-0129) and monocarboaluminate (PDF #00-036-0377). Hemicarboaluminate is  
174 often observed in low MgO-content samples (< 5 wt.% within the slag) at lower degree of  
175 reaction (i.e. early age), while monocarboaluminate is often observed in samples with  
176 moderate MgO content at later age<sup>20</sup>. Gaylussite (PDF #00-021-0343) is normally identified  
177 in sodium carbonate-activated slag pastes at early age as a transient phase<sup>20</sup>, consistent with  
178 its identification here only in the 28-day samples without CLDH addition in Figure 1. The  
179 180-day samples, and the 28-day samples with 5% CLDH addition, have higher content of  
180 hydrotalcite-like phases (PDF #00-014-0525) than the 28-day sample without CLDH addition.

181



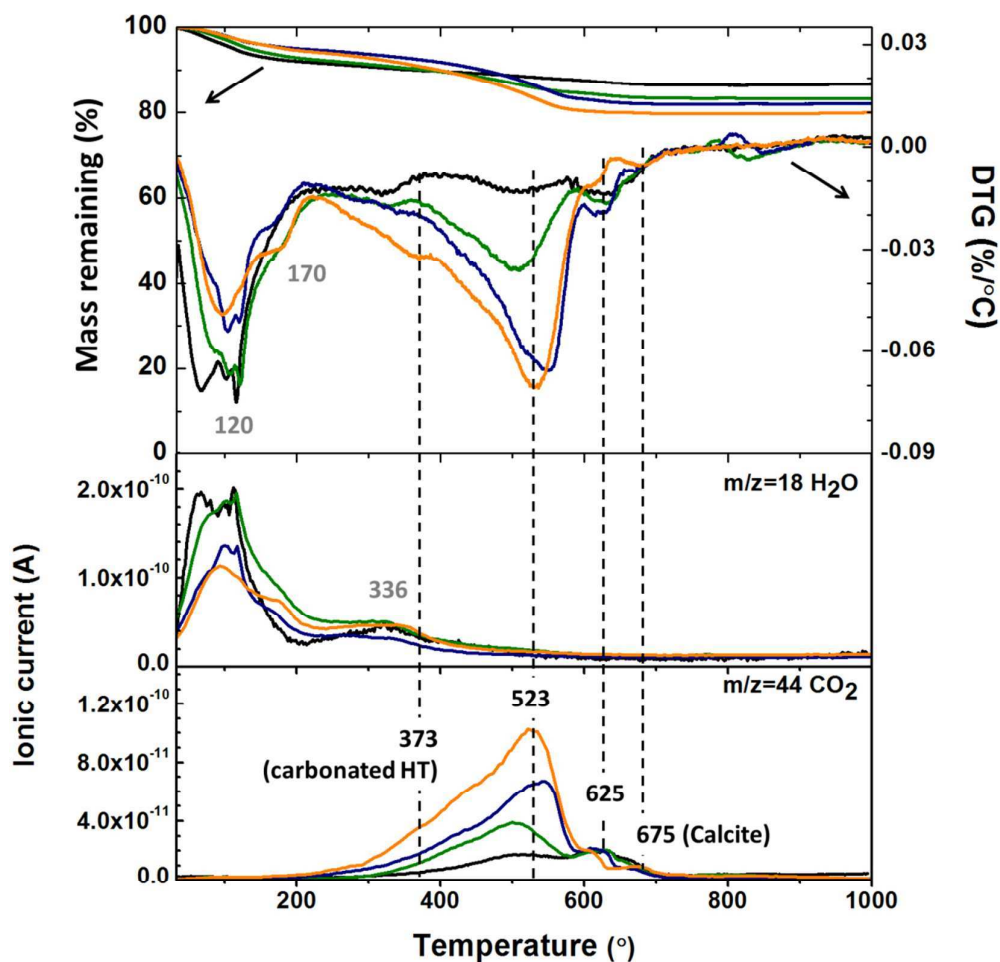


**Figure 1.** X-ray diffraction patterns of the sodium carbonate-activated slag pastes, after being exposed to 0% (non-carbonated), 0.04% (naturally carbonated) and 1.0% CO<sub>2</sub> (accelerated carbonated) for 24 hours. Phases marked are: Cs - calcium (sodium) aluminat silicate hydrate; C - calcite, V - vaterite; HT - hydrotalcite-like phase; Ga - gaylussite; Hc - hemicarboaluminate, Mc – monocarboaluminate. The inset on the left enlarges the low-angle region.

When the pastes were exposed to CO<sub>2</sub>, there was a significant increase in the content of two polymorphs of CaCO<sub>3</sub>: calcite (PDF# 00-005-0586) and vaterite (PDF# 00-033-0268), as a result of the decalcification of the C-(N)-A-S-H type gel<sup>28</sup> (Figure 1). The gaylussite present in the 28-day sample without CLDH did not seem to be influenced by carbonation, while the small fraction of hemicarboaluminate in the same sample seemed to have been carbonated to monocarboaluminate. A higher amount of both CaCO<sub>3</sub> polymorphs was formed under exposure to more aggressive carbonation concentrations, indicating a higher content of decalcification of the main reaction product, as observed in sodium silicate-activated slag cements<sup>28,33</sup>. The same trend has been observed in samples exposed to a more extended time of carbonation (see Supporting Information). At a higher extent of carbonation, whether achieved by increasing the CO<sub>2</sub> concentration and/or by extending the exposure time, the formation of vaterite seems to be favored over calcite. The precipitation of CaCO<sub>3</sub> polymorphs is known to be closely related to the activities of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>, as well as pH and concentrations of other dissolved ions in the aqueous phase<sup>34-36</sup>. The pH values at which different CaCO<sub>3</sub> polymorphs precipitate are different, and the addition of alkali (e.g. NaOH) could inhibit the precipitation of well-crystallized calcite<sup>36</sup>. When the carbonation process in an alkali-activated cement starts, the atmospheric CO<sub>2</sub> gradually dissolves in the alkaline pore solution (pH>13), consumes OH<sup>-</sup>, and leads to an increased concentration of CO<sub>3</sub><sup>2-</sup> in the

1  
2  
3 208 pore solution<sup>37</sup>. The decreased alkalinity of the pore solution destabilizes the C-(N)-A-S-H  
4 209 type gel, and results in increased  $\text{Ca}^{2+}$  concentration in the carbonated pore solution<sup>37-38</sup>. The  
5  
6 210 increased concentration of both  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  in the pore solution, together with decreased  
7  
8 211 pH, favors the formation of vaterite over calcite<sup>35</sup>.  
9  
10 212

11  
12 213 The samples cured for 180 days without CLDH addition appear to have the lowest amount  
13  
14 214 of calcium carbonate forming, suggesting the highest carbonation resistance under natural  
15  
16 215 carbonation conditions, likely due to the presence of higher amount of dense, space-filling  
17  
18 216 hydrous reaction product phases at extended times of curing<sup>20</sup>. Samples modified with 5 wt.%  
19  
20 217 CLDH have higher hydrotalcite-group phase content, which enables them to absorb  
21  
22 218 additional  $\text{CO}_2$  by its incorporation via substitution of hydroxide in these phases<sup>39-40</sup>. Figure  
23  
24 219 2 demonstrates this additional  $\text{CO}_2$  binding in the CLDH-containing sample by TG-MS:  
25  
26 220 compared with the paste without CLDH modification (blue line, Figure 2), the CLDH-  
27  
28 221 modified sample (orange line, Figure 2) showed a significantly higher mass loss centered at  
29  
30 222 around 373 °C caused by the release of  $\text{CO}_2$ , consistent with that which is observed from  
31  
32 223 carbonated hydrotalcite-like phases<sup>41</sup>. Additionally, the mass loss from these two samples  
33  
34 224 (blue and orange lines, Figure 2) below 200 °C, associated with the water loss from the main  
35  
36 225 reaction product C-(N)-A-S-H type gel, appeared to be similar. These observations may  
37  
38 226 indicate that the addition of CLDH enables the binder to take up a higher content of  $\text{CO}_2$   
39  
40 227 without damaging the main strength-giving reaction product phases.  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



228

229 **Figure 2.** TG-MS data for sodium carbonate-activated slag paste (28d, 0 wt.% CLDH)  
 230 exposed to 0% (black line), 0.04% (green line) and 1.0% CO<sub>2</sub> (blue line) for 24 hours, and a  
 231 CLDH modified sample (28d, 5 wt.% CLDH) exposed to 1.0% CO<sub>2</sub> for 24 hours (orange line)  
 232

233 As calcium carbonate salts form upon carbonation in sodium carbonate-activated slags,  
 234 their formation requires the release of calcium from the C-(N)-A-S-H type gels. So, the long  
 235 term stability of these materials will depend on the structural changes that take place in these  
 236 strength-giving phases<sup>28</sup>, and the changes in microstructure that may alter the pore volume  
 237 and connectivity<sup>31</sup>. These factors therefore need further investigation, as discussed in the  
 238 following sections.

239

240

241

242

## 243        **Structural changes in calcium aluminosilicate hydrate type gels**

244

245        The main reaction product in these cements is a sodium-rich calcium aluminosilicate  
246 hydrate (C-(N)-A-S-H) type gel, which has a disordered tobermorite-like structure consisting  
247 of dreierketten silicate chain units, and with some of the Si sites substituted by Al<sup>42-43</sup>. Solid-  
248 state <sup>29</sup>Si and <sup>27</sup>Al magic angle spinning nuclear magnetic resonance (MAS NMR)  
249 spectroscopy provides valuable information to identify changes in the coordination  
250 environments of Si and Al atoms within this gel, as a consequence of carbonation.

251

252        In the <sup>29</sup>Si MAS NMR spectra (Figure 3), three distinct resonance at -79 ppm, -82 ppm  
253 and -85 ppm were identified in non-carbonated slag pastes with or without CLDH after 28  
254 and 180 days of curing; these are assigned to Q<sup>1</sup>, Q<sup>2</sup>(1Al) and Q<sup>2</sup> sites within the C-(N)-A-S-  
255 H type gel<sup>44</sup>. The broad resonance centered at -74 ppm is attributed to the fraction of  
256 unreacted slag, mainly consisting of Q<sup>0</sup> and some Q<sup>1</sup> and Q<sup>2</sup> sites (Figure 3D). The  
257 assignments of these silica sites were chosen in accordance with the previous study of Ke et  
258 al.<sup>20</sup>, where samples of corresponding composition were prepared and characterized. After  
259 24 hours of exposure to natural carbonation (green lines in Figure 3), decreased intensity of  
260 the Q<sup>1</sup> and Q<sup>2</sup>(1Al) sites, along with an increase in the intensity of the Q<sup>2</sup> resonance, were  
261 observed. Samples exposed to 1.0% CO<sub>2</sub> for 24 hours underwent much more significant  
262 structural changes as a result of exposure to this higher CO<sub>2</sub> concentration (blue lines). A  
263 significant decrease in all chain-type silicate environments was observed, while an intense  
264 but broad band centered at around -95 ppm appeared. The chemical shift of this site correlates  
265 with crosslink-type silica sites (Q<sup>3</sup>) or tetrahedral silica coordinated in part by Al (most likely  
266 Q<sup>4</sup>(2Al))<sup>45</sup>.

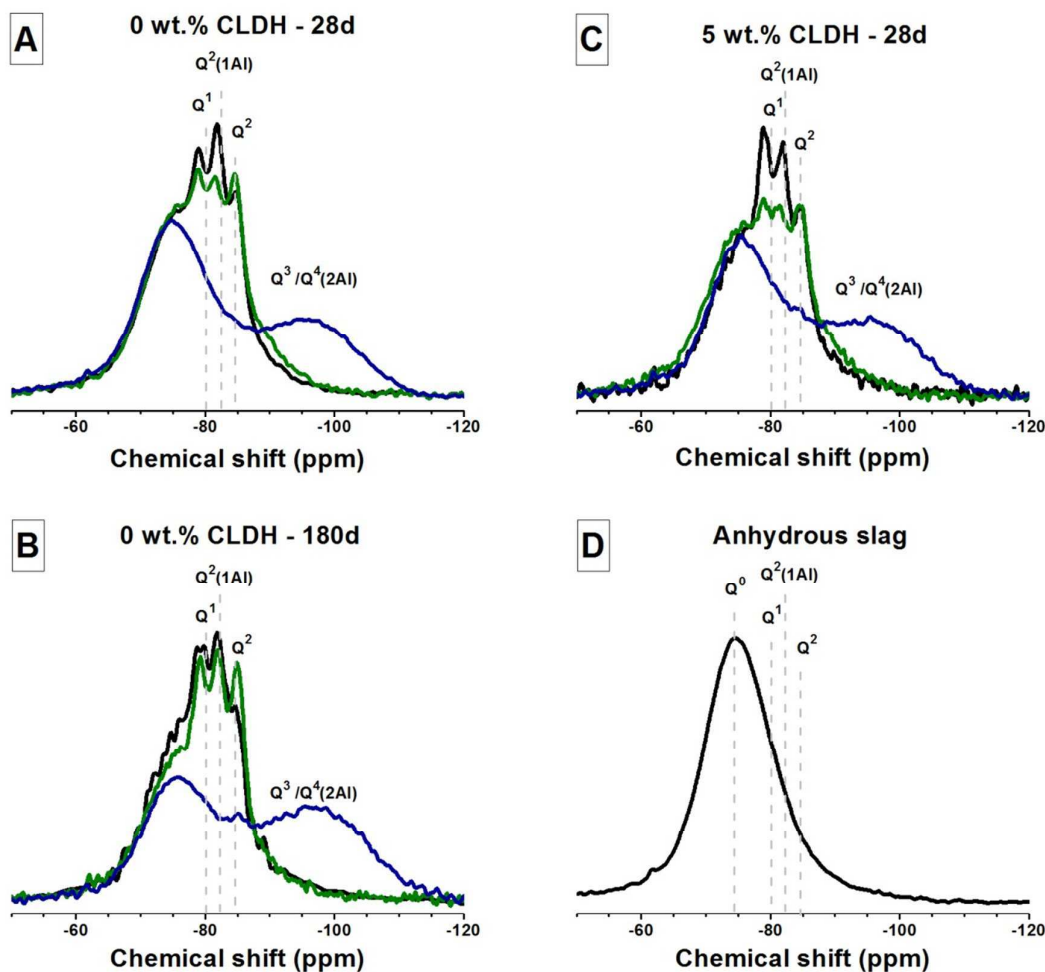
267

268        Comparing the <sup>29</sup>Si MAS NMR spectra of the various samples exposed to 0.04% CO<sub>2</sub> for  
269 24 hours (Figure 3), it appears that the decalcification process starts with the loss of interlayer  
270 Ca, that was initially charge balancing either end-chain Q<sup>1</sup> site or Q<sup>2</sup>(1Al) sites. This enables  
271 the un-balanced silica sites to bridge with the neighboring un-balanced silica sites, thus  
272 increasing the content of crosslinked or network silica sites (i.e. Q<sup>3</sup> or Q<sup>4</sup>). These mechanisms  
273 are consistent with the observed increase in connectivity of the C-(N)-A-S-H type gel after

1  
2  
3 274 carbonation, similar to that which is identified in C-S-H type gels<sup>46</sup>, which decompose to a  
4 275 crosslinked silica gel plus calcium carbonate under similar exposure conditions.  
5  
6  
7 276

8  
9 277 The loss of the chain-like structure of the C-(N)-A-S-H gel upon carbonation, particularly  
10 278 at high CO<sub>2</sub> concentrations (1.0% CO<sub>2</sub>), is also similar to the behavior observed in carbonated  
11 279 sodium silicate<sup>28, 38, 40</sup> and sodium hydroxide-activated slag pastes<sup>38</sup>, where the continuous  
12 280 loss of Q<sup>1</sup> and Q<sup>2</sup> silica sites is associated with a higher extent of carbonation. It appears that  
13 281 the C-(N)-A-S-H type gel in the sodium carbonate activated slag paste cured for 180 days  
14 282 prior to carbonation was more stable than the gels which formed in either of the 28-day cured  
15 283 samples (Figure 3, with or without CLDH), consistent with observations from XRD (Figure 1,  
16 284 and Supporting Information). However, the addition of CLDH did not seem to have  
17 285 significantly altered the residual C-(N)-A-S-H structure formed upon carbonation (comparing  
18 286 Figure 3A and C), although there was more CO<sub>2</sub> absorbed in the binder (Figure 2).  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60

287



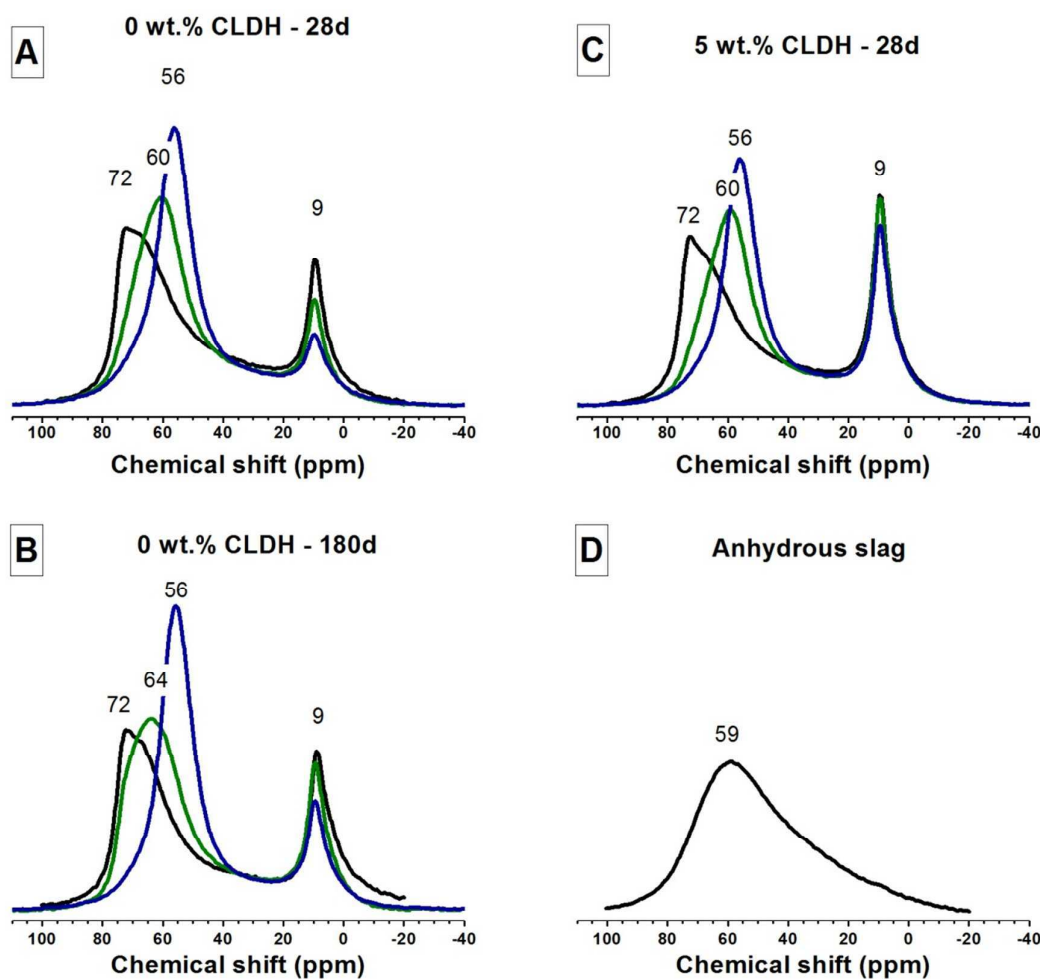
288

289 **Figure 3.**  $^{29}\text{Si}$  MAS NMR spectra of sodium carbonate-activated slag pastes exposed to 0%  
 290 (black line), 0.04% (green line) and 1.0%  $\text{CO}_2$  (blue line) for 24 hours. Results for non-  
 291 carbonated samples are from <sup>20</sup>.  
 292

293 Two distinct Al environments were identified from the  $^{27}\text{Al}$  MAS NMR results in Figure 4.  
 294 The resonance at around 60-80 ppm corresponds to  $\text{Al}^{\text{IV}}$  and is assigned to the tetrahedral Al  
 295 environments in C-(N)-A-S-H type gel (also partially contributed by unreacted slag), and the  
 296  $\text{Al}^{\text{VI}}$  resonances at chemical shift values below 20 ppm are assigned to the Al sites in the  
 297 two types of LDH structures present (Mg-Al and AFm) <sup>44-45</sup>. The chemical shift of  
 298 tetrahedrally-coordinated Al decreases at a higher degree of crosslinking. The  $^{27}\text{Al}$  MAS  
 299 NMR resonance of  $\text{Al}^{\text{IV}}$  in chain-type aluminosilicates normally appears at between 70 ppm  
 300 to 80 ppm, while in tetrahedral framework aluminosilicates this peak appears at between 55  
 301 to 68 ppm <sup>45</sup>. The shift of the  $\text{Al}^{\text{IV}}$  peak in Figure 4 therefore suggests the release of  $\text{Al}^{\text{IV}}$   
 302 from C-(N)-A-S-H type gel, and formation of a more highly cross-linked aluminosilicate type  
 303 gel. Correlating this result with the observation of the  $^{29}\text{Si}$  MAS NMR spectra in Figure 3, the

304 broad chemical shift of Al<sup>[IV]</sup> centered at around 60 ppm in samples exposed to 0.04% CO<sub>2</sub> is  
 305 likely to be contributed mainly by Al in cross-linked C-(N)-A-S-H type gel, as only a small  
 306 fraction of highly crosslinked Si sites were formed. However, for samples exposed to 1.0%  
 307 CO<sub>2</sub>, where a large fraction of cross-linked Si sites was identified, the intense and narrow  
 308 band centered at 56 ppm (Figure 4) identified in all samples indicates the presence of Al<sup>[IV]</sup> in  
 309 Q<sup>4</sup> sites with largely similar coordination environments, similar to that identified in sodium-  
 310 aluminosilicate geopolymers<sup>47-48</sup>.

311



312

313 **Figure 4.**<sup>27</sup>Al MAS NMR spectra of sodium carbonate-activated slag pastes (curing  
 314 conditions as marked), exposed to 0% (black line), 0.04% (green line) and 1.0% CO<sub>2</sub> (blue  
 315 line) for 24 hours, and the spectrum of the unreacted slag. Results for non-carbonated  
 316 samples are from<sup>20</sup>.

317

1  
2  
3 318 The decrease in the relative intensities of the Al<sup>[VI]</sup> band at 9 ppm in Figure 4 as a result of  
4 319 carbonation is caused by the decomposition of AFm phases at the lower pH induced by  
5 320 carbonation<sup>49-50</sup>, in agreement with the disappearance of AFm phases from the XRD data in  
6 321 Figure 1 after carbonation. The alumina released from the decomposed AFm phase might  
7 322 also become incorporated into the highly cross-linked aluminosilicate gel. In comparison, the  
8 323 hydrotalcite-like Mg-Al LDH is much more stable when exposed to carbonation, and so  
9 324 samples with 5% CLDH showed the least decrease in the Al<sup>[VI]</sup> band.  
10  
11  
12  
13  
14  
15

325

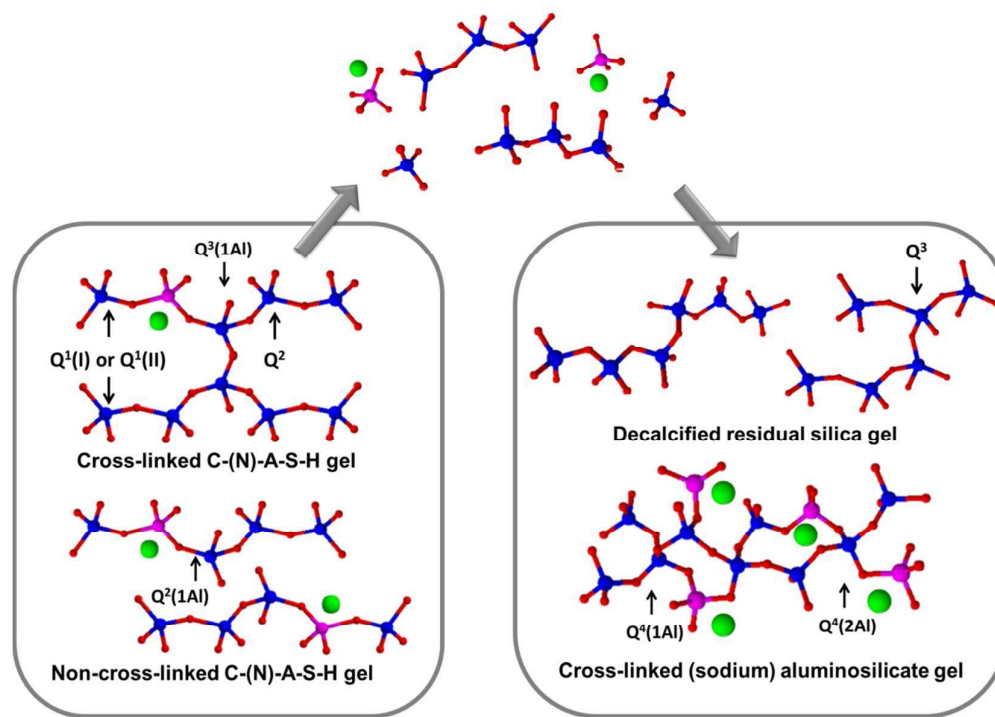
16 326 Some fraction of the unreacted slag may also react with CO<sub>2</sub> during the carbonation  
17 327 process. However, this process has been observed to take place very slowly unless under high  
18 328 temperature and high CO<sub>2</sub> pressure<sup>51</sup>, or in an aqueous solution preferably with higher  
19 329 alkalinity<sup>52-53</sup>. In AACs, the carbonation reaction would be expected to start from the gel  
20 330 binder phases between the slag grains first, and it would require a long time of exposure  
21 331 before having a significant influence on the unreacted slag grains<sup>33</sup>. Therefore, the main  
22 332 structural changes should be considered to take place in the gel binder phases.  
23  
24  
25  
26  
27  
28

333

29  
30  
31 334 A proposed scheme of structural changes in sodium carbonate activated slag paste during  
32 335 the carbonation process is illustrated in Figure 5.  
33  
34

336





337

338 **Figure 5.** Structural changes in sodium carbonate activated slag paste during carbonation,  
 339 where the blue balls represent Si, the pink balls represent Al, the red balls represent O, and  
 340 the green balls represent Na.  
 341

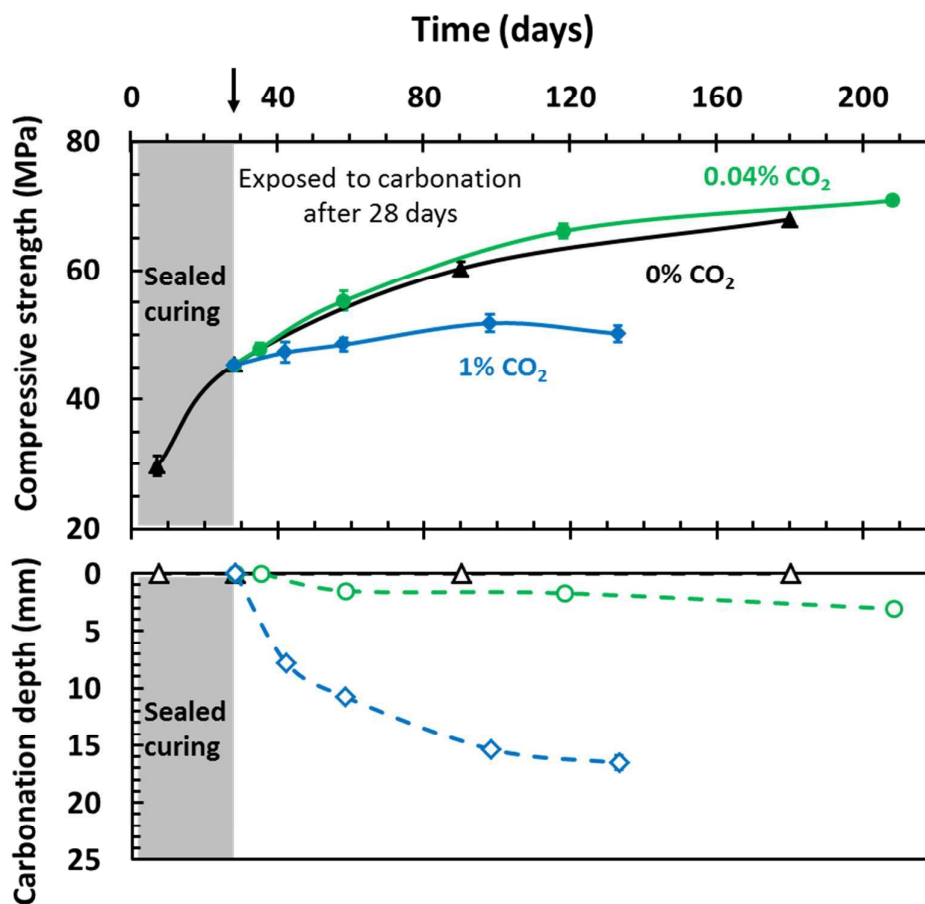
### 342 The potential for effective carbon sequestration

343 If carbonation of these cements is to be considered as a useful carbon sink, an essential  
 344 prerequisite is that there is not a loss of performance (strength or durability-related  
 345 characteristics) as a result of this process. Figure 6 shows the changes in compressive  
 346 strength of mortar cubes cured for 28 days and exposed to different carbonation conditions.  
 347 The increase in the strength of non-carbonated (0%  $CO_2$ ) samples was contributed by the  
 348 increased degree of slag reaction over time<sup>21</sup>. In comparison, samples exposed to natural  
 349 carbonation conditions (0.04%  $CO_2$ ) exhibited essentially the same strength evolution, at the  
 350 low extent of carbonation reached. For samples exposed to accelerated carbonation  
 351 conditions (1%  $CO_2$ ), the compressive strength remained relatively constant at the level  
 352 reached after 28 days of sealed curing, and the greater carbonation depth indicated a much  
 353 higher extent of carbonation. Samples with 5% CLDH showed very similar strength  
 354 performance to these 0% CLDH samples at the longest carbonation exposure time measured  
 355 (see Supporting Information, Figure S4). The higher compressive strengths of 5% CLDH

1  
2  
3 356 samples at early age were induced by the influence of CLDH <sup>21</sup>, which does not seem to  
4 357 influence long-term strength performance under carbonation.  
5  
6  
7 358

8  
9 359 As explained previously, the adoption of accelerated testing conditions was intended to  
10 360 simulate years of CO<sub>2</sub> exposure under a natural atmosphere; therefore the lower compressive  
11 361 strength obtained from the samples after accelerated carbonation might not occur even after  
12 362 years of ambient exposure. The continuing development of strength as a result of the  
13 363 ongoingly increasing degree of reaction of the cement under natural carbonation conditions  
14 364 would also be expected to densify the cementitious matrix over the years, making it less  
15 365 permeable to the carbon dioxide.  
16  
17  
18  
19  
20  
21 366

22 367 The strength evolution of sodium carbonate activated slag mortar upon carbonation is  
23 368 opposite to that observed in sodium silicate-activated slag mortars, where the compressive  
24 369 strength has been observed to decrease significantly with increased carbonation depth as the  
25 370 result of increased pore volumes <sup>54</sup>. However in the sodium carbonate-activated system, the  
26 371 overall intrudable porosity decreased after carbonation (see Supporting Information for MIP  
27 372 results), suggesting that the precipitation of calcium carbonates might have blocked the  
28 373 connected pores, similar to carbonation behaviors that have been reported for PC <sup>55</sup>.  
29  
30  
31  
32  
33  
34 374  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



375

376 **Figure 6.** Changes in compressive strength of sodium carbonate activated slag mortar and  
 377 corresponding carbonation depths, after exposure to different carbonation conditions. All  
 378 samples were cured for 28 days in sealed plastic bags before carbonation exposure.  
 379

380 It has previously been shown that alkali-activated binders subjected to natural carbonation  
 381 are able to retain sufficient alkalinity that steel corrosion is not necessarily going to be  
 382 initiated, even once the carbonation front has passed the steel-concrete interface<sup>56-58</sup>. The  
 383 total carbon uptake of a cementitious material during its life cycle accumulates with time,  
 384 where a longer service life is normally associated with higher CO<sub>2</sub> uptake<sup>25</sup>. The degradation  
 385 in mechanical strength that normally takes place in sodium silicate-activated slag cement  
 386 upon carbonation<sup>30-31</sup> was not observed in sodium carbonate-activated slag cements,  
 387 suggesting that the sodium carbonate-activated slag cement could have a longer service life  
 388 under atmospheric carbonation conditions without degradation in its performance, while  
 389 taking up a modest quantity of CO<sub>2</sub> (Figure 3) into its structure and giving some degree of  
 390 carbon sequestration.

391

## 392 **Conclusions**

393

394 Carbonation of sodium carbonate-activated slag cements under natural and accelerated  
395 conditions results in both the formation of calcium carbonate (as both vaterite and calcite  
396 polymorphs), and structural changes in the strength-giving cement hydrate phases. An  
397 assemblage of decalcified C-S-H type gel and cross-linked alkali aluminosilicate gel were  
398 formed as a result of decalcification of the C-(N)-A-S-H type gel which is the main binding  
399 phase in these cements. The incorporation of a calcined hydrotalcite-like layered double  
400 hydroxide (CLDH) increases the capacity for uptake of CO<sub>2</sub> into these binders in service,  
401 without bringing changes to the structures of the main reaction products. Unlike some other  
402 alkali-activated slag cements, which have been described in the literature, the sodium  
403 carbonate-activated slag cements investigated here maintain their mechanical strength upon  
404 carbonation.

405

## 406 **Acknowledgments**

407 This research was funded by the European Research Council under the European Union's  
408 Seventh Framework Programme (FP7/2007-2013) / ERC Grant Agreement #335928  
409 (GeopolyConc). The participation of SAB in this research was partially funded by the UK  
410 Engineering and Physical Sciences Research Council (EPSRC) through grant EP/M003272/1.  
411 Solid-state NMR spectra were obtained at the EPSRC UK National Solid-state NMR Service  
412 at Durham. The technical support provided by Dr. Oday H. Hussein is also greatly  
413 acknowledged.

## 414 **Supporting Information**

415 The following contents are provided as Supporting Information:

- 416 - XRD patterns of the phase evolution of three samples assessed as a function of CO<sub>2</sub>  
417 concentration (0.04 % and 1.0 %), and exposure time (from 4 hours up to 14 days);
- 418 - Compressive strength of sodium carbonate activated slag mortars (with 5% CLDH,  
419 sealed for 28 days) after exposure to different carbonation conditions
- 420 - Differential pore volume distributions in carbonated mortar fractions measured using  
421 MIP

**References**

1. Juenger, M. C. G.; Winnefeld, F.; Provis, J. L.; Ideker, J. H., Advances in alternative cementitious binders. *Cem. Concr. Res.* **2011**, *41*, 1232-1243. DOI 10.1016/j.cemconres.2010.11.012
2. Provis, J. L.; Bernal, S. A., Geopolymers and related alkali-activated materials. *Annu. Rev. Mater. Res.* **2014**, *44*, 299-327. DOI 10.1146/annurev-matsci-070813-113515
3. Bernal, S. A.; Provis, J. L.; Fernández-Jiménez, A.; Krivenko, P. V.; Kavalerova, E.; Palacios, M.; Shi, C., Binder chemistry–high-calcium alkali-activated materials. In: *Alkali-Activated Materials, State of the Art Report of RILEM TC 224-AAM*, Dordrecht, Springer: 2014; pp 59-91. DOI 10.1007/978-94-007-7672-2\_3
4. Fernández-Jiménez, A.; Puertas, F., Setting of alkali-activated slag cement. Influence of activator nature. *Adv. Cem. Res.* **2001**, *13*, 115-121. DOI 10.1680/adcr.2001.13.3.11
5. Bernal, S. A.; San Nicolas, R.; van Deventer, J. S. J.; Provis, J. L., Alkali-activated slag cements produced with a blended sodium carbonate/silicate activator. *Adv. Cem. Res.* **2015**, *28*, 262-273. DOI 10.1680/jadcr.15.00013
6. Duran Atiş, C.; Bilim, C.; Çelik, Ö.; Karahan, O., Influence of activator on the strength and drying shrinkage of alkali-activated slag mortar. *Constr. Build. Mater.* **2009**, *23*, 548-555. DOI 10.1016/j.conbuildmat.2007.10.011
7. Provis, J. L., Green concrete or red herring? – future of alkali-activated materials. *Adv. Appl. Ceram.* **2014**, *113*, 472-477. DOI 10.1179/1743676114Y.0000000177
8. Habert, G.; d’Espinose de Lacaillerie, J. B.; Roussel, N., An environmental evaluation of geopolymer based concrete production: reviewing current research trends. *J. Cleaner Prod.* **2011**, *19*, 1229-1238. DOI 10.1016/j.jclepro.2011.03.012
9. Habert, G.; Ouellet-Plamondon, C., Recent update on the environmental impact of geopolymers. *RILEM Techn. Lett.* **2016**, *1*, 17-23. DOI 10.21809/rilemtechlett.2016.6
10. Fawer, M.; Concannon, M.; Rieber, W., Life cycle inventories for the production of sodium silicates. *Int. J. Life Cycle Assessment* **1999**, *4*, 207-212. DOI 10.1007/bf02979498
11. Sharma, B. K., *Industrial Chemistry*. GOEL Publishing House, Delhi: 1991.

- 1  
2  
3 450 12. Kostick, D. S. *2011 Minerals Yearbook*; U.S. Department of the Interior, U.S.  
4 451 Geological Survey, Washington DC: 2012.  
5  
6  
7 452 13. Office of Air and Radiation, Technical support document for the soda ash  
8 453 manufacturing sector: proposed rule for mandatory reporting of greenhouse gases. United  
9 454 States EPA, Washington DC, 2009.  
10  
11  
12 455 14. Bai, Y.; Collier, N.; Milestone, N.; Yang, C., The potential for using slags activated  
13 456 with near neutral salts as immobilisation matrices for nuclear wastes containing reactive  
14 457 metals. *J. Nucl. Mater.* **2011**, *413*, 183-192. DOI 10.1016/j.jnucmat.2011.04.011  
15  
16  
17  
18 458 15. Escalante-García, J. I.; Fuentes, A. F.; Gorokhovskiy, A.; Fraire-Luna, P. E.;  
19 459 Mendoza-Suarez, G., Hydration products and reactivity of blast-furnace slag activated by  
20 460 various alkalis. *J. Am. Ceram. Soc.* **2003**, *86*, 2148-2153. DOI 10.1111/j.1151-  
21 461 2916.2003.tb03623.x  
22  
23  
24  
25  
26 462 16. Glukhovskiy, V. D.; Krivenko, P. V.; Rostovskaya, G. S.; Timkovich, V. J.;  
27 463 Pankratov, V. L., Binder. United States Patent 4,410,365, 1983.  
28  
29  
30 464 17. Bernal, S. A.; Provis, J. L.; Myers, R. J.; San Nicolas, R.; van Deventer, J. S. J., Role  
31 465 of carbonates in the chemical evolution of sodium carbonate-activated slag binders. *Mater.*  
32 466 *Struct.* **2014**, *48*, 517-529. DOI 10.1617/s11527-014-0412-6  
33  
34  
35  
36 467 18. Wang, S.-D.; Scrivener, K. L.; Pratt, P. L., Factors affecting the strength of alkali-  
37 468 activated slag. *Cem. Concr. Res.* **1994**, *24*, 1033-1043. DOI 10.1016/0008-8846(94)90026-4  
38  
39  
40 469 19. Fernández-Jiménez, A.; Puertas, F., Effect of activator mix on the hydration and  
41 470 strength behaviour of alkali-activated slag cements. *Adv. Cem. Res.* **2003**, *15*, 129-136. DOI  
42 471 10.1680/adcr.2003.15.3.129  
43  
44  
45  
46 472 20. Ke, X.; Bernal, S. A.; Provis, J. L., Controlling the reaction kinetics of sodium  
47 473 carbonate-activated slag cements using calcined layered double hydroxides. *Cem. Concr. Res.*  
48 474 **2016**, *81*, 24-37. DOI 10.1016/j.cemconres.2015.11.012  
49  
50  
51  
52 475 21. Ke, X.; Bernal, S. A.; Hussein, O. H.; Provis, J. L., Chloride binding and mobility in  
53 476 sodium carbonate-activated slag pastes and mortars. *Mater. Struct.* **2017**, *50*, #252. DOI  
54 477 10.1617/s11527-017-1121-8  
55  
56  
57  
58  
59  
60

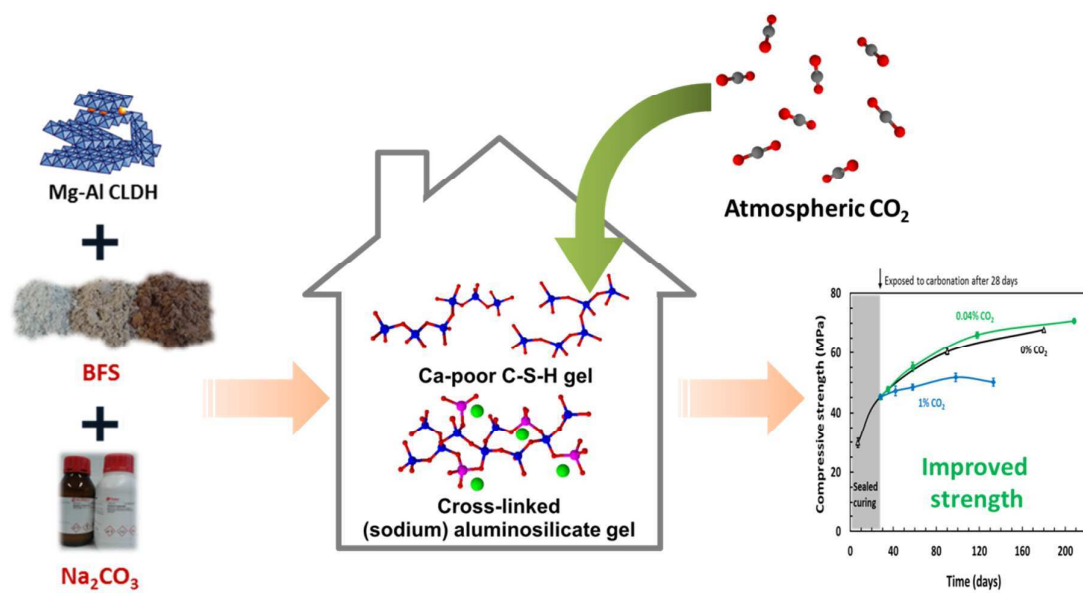
- 1  
2  
3 478 22. Fernández-Bertos, M.; Simons, S. J. R.; Hills, C. D.; Carey, P. J., A review of  
4 479 accelerated carbonation technology in the treatment of cement-based materials and  
5  
6 480 sequestration of CO<sub>2</sub>. *J. Hazard. Mater.* **2004**, *B112*, 193-205. DOI  
7  
8 481 10.1016/j.jhazmat.2004.04.019  
9  
10 482 23. Sanjuán, M. A.; Andrade, C.; Cheyrezy, M., Concrete carbonation test in natural and  
11  
12 483 accelerated conditions. *Adv. Cem. Res.* **2003**, *15*, 171 - 180. DOI 10.1680/adcr.2003.15.4.171  
13  
14 484 24. Hobbs, D. W., Concrete deterioration: causes, diagnosis, and minimising risk. *Int.*  
15  
16 485 *Mater. Rev.* **2001**, *46*, 117-144. DOI 10.1179/095066001101528420  
17  
18 486 25. Xi, F.; Davis, S. J.; Ciais, P.; Crawford-Brown, D.; Guan, D.; Pade, C.; Shi, T.;  
19  
20 487 Syddall, M.; Lv, J.; Ji, L.; Bing, L.; Wang, J.; Wei, W.; Yang, K.-H.; Lagerblad, B.; Galan, I.;  
21  
22 488 Andrade, C.; Zhang, Y.; Liu, Z., Substantial global carbon uptake by cement carbonation.  
23  
24 489 *Nat. Geosci.* **2016**, *9*, 880-883. DOI 10.1038/ngeo2840  
25  
26 490 26. Taylor, H. F. W., *Cement Chemistry*. Thomas Telford, London: 1997.  
27  
28 491 27. Puertas, F.; Fernández-Jiménez, A.; Blanco-Varela, M. T., Pore solution in alkali-  
29  
30 492 activated slag cement pastes. Relation to the composition and structure of calcium silicate  
31  
32 493 hydrate. *Cem. Concr. Res.* **2004**, *34*, 139-148. DOI 10.1016/S0008-8846(03)00254-0  
33  
34 494 28. Bernal, S. A.; Provis, J. L.; Walkley, B.; San Nicolas, R.; Gehman, J. D.; Brice, D. G.;  
35  
36 495 Kilcullen, A. R.; Duxson, P.; van Deventer, J. S. J., Gel nanostructure in alkali-activated  
37  
38 496 binders based on slag and fly ash, and effects of accelerated carbonation. *Cem. Concr. Res.*  
39  
40 497 **2013**, *53*, 127-144. DOI 10.1016/j.cemconres.2013.06.007  
41  
42 498 29. Xu, H.; Provis, J. L.; van Deventer, J. S. J.; Krivenko, P. V., Characterization of aged  
43  
44 499 slag concretes. *ACI Mater. J.* **2008**, *105*, 131-139. DOI 10.14359/19753  
45  
46 500 30. Bernal, S. A.; Mejía de Gutierrez, R.; Provis, J. L.; Rose, V., Effect of silicate  
47  
48 501 modulus and metakaolin incorporation on the carbonation of alkali silicate-activated slags.  
49  
50 502 *Cem. Concr. Res.* **2010**, *40*, 898-907. DOI 10.1016/j.cemconres.2010.02.003  
51  
52 503 31. Puertas, F.; Palacios, M.; Vázquez, T., Carbonation process of alkali-activated slag  
53  
54 504 mortars. *J. Mater. Sci.* **2006**, *41*, 3071-3082. DOI 10.1007/s10853-005-1821-2  
55  
56  
57  
58  
59  
60

- 1  
2  
3 505 32. British Standards Institute, BS EN 196-1:2005 Methods of testing cement. Part 1:  
4 506 Determination of strength, London, UK, 2005.
- 5  
6  
7 507 33. Bernal, S. A.; San Nicolas, R.; Provis, J. L.; Mejía de Gutiérrez, R.; van Deventer, J.  
8 508 S. J., Natural carbonation of aged alkali-activated slag concretes. *Mater. Struct.* **2014**, *47*,  
9 509 693-707. DOI 10.1617/s11527-013-0089-2
- 10  
11  
12 510 34. Jun, K.; Norimasa, S.; Akira, M.; Masao, K., Precipitation diagram of calcium  
13 511 carbonate polymorphs: its construction and significance. *J. Phys.: Condens. Matter* **2009**, *21*,  
14 512 425102. DOI 10.1088/0953-8984/21/42/425102
- 15  
16  
17  
18 513 35. Han, Y. S.; Hadiko, G.; Fuji, M.; Takahashi, M., Crystallization and transformation of  
19 514 vaterite at controlled pH. *J. Cryst. Growth* **2006**, *289*, 269-274. DOI  
20 515 10.1016/j.jcrysgro.2005.11.011
- 21  
22  
23  
24 516 36. Gal, J.-Y.; Bollinger, J.-C.; Tolosa, H.; Gache, N., Calcium carbonate solubility: a  
25 517 reappraisal of scale formation and inhibition. *Talanta* **1996**, *43*, 1497-1509. DOI  
26 518 10.1016/0039-9140(96)01925-X
- 27  
28  
29  
30 519 37. Bernal, S. A.; Provis, J. L.; Brice, D. G.; Kilcullen, A.; Duxson, P.; van Deventer, J.  
31 520 S. J., Accelerated carbonation testing of alkali-activated binders significantly underestimates  
32 521 service life: The role of pore solution chemistry. *Cem. Concr. Res.* **2012**, *42*, 1317-1326. DOI  
33 522 10.1016/j.cemconres.2012.07.002
- 34  
35  
36  
37 523 38. Palacios, M.; Puertas, F., Effect of carbonation on alkali-activated slag paste. *J. Am.*  
38 524 *Ceram. Soc.* **2006**, *89*, 3211-3221. DOI 10.1111/j.1551-2916.2006.01214.x
- 39  
40  
41  
42 525 39. Dadwhal, M.; Kim, T. W.; Sahimi, M.; Tsotsis, T. T., Study of CO<sub>2</sub> diffusion and  
43 526 adsorption on calcined layered double hydroxides: the effect of particle size. *Ind. Eng. Chem.*  
44 527 *Res.* **2008**, *47*, 6150-6157. DOI 10.1021/ie701701d
- 45  
46  
47  
48 528 40. Bernal, S. A.; San Nicolas, R.; Myers, R. J.; Mejía de Gutiérrez, R.; Puertas, F.; van  
49 529 Deventer, J. S. J.; Provis, J. L., MgO content of slag controls phase evolution and structural  
50 530 changes induced by accelerated carbonation in alkali-activated binders. *Cem. Concr. Res.*  
51 531 **2014**, *57*, 33-43. DOI 10.1016/j.cemconres.2013.12.003
- 52  
53  
54  
55  
56  
57  
58  
59  
60



- 1  
2  
3 532 41. Ke, X.; Bernal, S. A.; Provis, J. L., Uptake of chloride and carbonate by Mg-Al and  
4 533 Ca-Al layered double hydroxides in simulated pore solutions of alkali-activated slag cement.  
5 534 *Cem. Concr. Res.* **2017**, *100*, 1-13. DOI 10.1016/j.cemconres.2017.05.015  
6  
7  
8 535 42. Faucon, P.; Delagrave, A.; Richet, C.; Marchand, J. M.; Zanni, H., Aluminum  
9 536 incorporation in calcium silicate hydrates (C-S-H) depending on their Ca/Si ratio. *J. Phys.*  
10 537 *Chem. B* **1999**, *103*, 7796-7802. DOI 10.1021/jp990609q  
11  
12  
13  
14 538 43. Richardson, I. G.; Brough, A. R.; Groves, G. W.; Dobson, C. M., The characterization  
15 539 of hardened alkali-activated blast-furnace slag pastes and the nature of the calcium silicate  
16 540 hydrate (C-S-H) phase. *Cem. Concr. Res.* **1994**, *24*, 813-829. DOI 10.1016/0008-  
17 541 8846(94)90002-7  
18  
19  
20  
21 542 44. Wang, S.-D.; Scrivener, K. L., <sup>29</sup>Si and <sup>27</sup>Al NMR study of alkali-activated slag. *Cem.*  
22 543 *Concr. Res.* **2003**, *33*, 769-774. DOI 10.1016/S0008-8846(02)01044-X  
23  
24  
25  
26 544 45. Engelhardt, G.; Michel, D., *High-Resolution Solid-State NMR of Silicates and*  
27 545 *Zeolites*. John Wiley & Sons: Chichester, 1987.  
28  
29  
30 546 46. Sevelsted, T. F.; Skibsted, J., Carbonation of C-S-H and C-A-S-H samples studied  
31 547 by <sup>13</sup>C, <sup>27</sup>Al and <sup>29</sup>Si MAS NMR spectroscopy. *Cem. Concr. Res.* **2015**, *71*, 56-65. DOI  
32 548 10.1016/j.cemconres.2015.01.019  
33  
34  
35  
36 549 47. Melar, J.; Renaudin, G.; Leroux, F.; Hardy-Dessources, A.; Nedelec, J.-M.; Taviot-  
37 550 Gueho, C.; Petit, E.; Steins, P.; Poulesquen, A.; Frizon, F., The porous network and its  
38 551 interface inside geopolymers as a function of alkali cation and aging. *J. Phys. Chem. C* **2015**,  
39 552 *119*, 17619-17632. DOI 10.1021/acs.jpcc.5b02340  
40  
41  
42  
43 553 48. Duxson, P.; Provis, J. L.; Lukey, G. C.; Separovic, F.; van Deventer, J. S. J., <sup>29</sup>Si  
44 554 NMR study of structural ordering in aluminosilicate geopolymer gels. *Langmuir* **2005**, *21*,  
45 555 3028-3036. DOI 10.1021/la047336x  
46  
47  
48  
49 556 49. Runcevski, T.; Dinnebier, R. E.; Magdysyuk, O. V.; Pollmann, H., Crystal structures  
50 557 of calcium hemicarboaluminate and carbonated calcium hemicarboaluminate from  
51 558 synchrotron powder diffraction data. *Acta Crystallogr. B* **2012**, *68*, 493-500. DOI  
52 559 10.1107/S010876811203042X  
53  
54  
55  
56  
57  
58  
59  
60

- 1  
2  
3 560 50. Mesbah, A.; Cau-dit-Coumes, C.; Renaudin, G.; Frizon, F.; Leroux, F., Uptake of  
4 561 chloride and carbonate ions by calcium monosulfoaluminate hydrate. *Cem. Concr. Res.* **2012**,  
5 562 *42*, 1157-1165. DOI 10.1016/j.cemconres.2012.05.012  
6  
7  
8  
9 563 51. Yu, J.; Wang, K., Study on characteristics of steel slag for CO<sub>2</sub> capture. *Energy &*  
10 564 *Fuels* **2011**, *25*, 5483-5492. DOI 10.1021/ef2004255  
11  
12  
13 565 52. Huijgen, W. J. J.; Comans, R. N. J., Carbonation of steel slag for CO<sub>2</sub> sequestration:  
14 566 leaching of products and reaction mechanisms. *Environ. Sci. Technol.* **2006**, *40*, 2790-2796.  
15 567 DOI 10.1021/es052534b  
16  
17  
18 568 53. Kasina, M.; Kowalski, P. R.; Michalik, M., Mineral carbonation of metallurgical  
19 569 slags. *Mineralogia*, **2015**, *45*, 27-45. DOI 10.1515/mipo-2015-0002  
20  
21  
22  
23 570 54. Bernal, S. A.; Mejía de Gutiérrez, R.; Provis, J. L., Engineering and durability  
24 571 properties of concretes based on alkali-activated granulated blast furnace slag/metakaolin  
25 572 blends. *Constr. Build. Mater.* **2012**, *33*, 99-108. DOI 10.1016/j.conbuildmat.2012.01.017  
26  
27  
28  
29 573 55. Tuutti, K., *Corrosion of steel in concrete*. Kungliga Tekniska Högskolan i Stockholm:  
30 574 CBI Forskning 82:4, 1982.  
31  
32  
33 575 56. Pouhet, R.; Cyr, M., Carbonation in the pore solution of metakaolin-based  
34 576 geopolymer. *Cem. Concr. Res.* **2016**, *88*, 227-235. DOI 10.1016/j.cemconres.2016.05.008  
35  
36  
37 577 57. Badar, M. S.; Kupwade-Patil, K.; Bernal, S. A.; Provis, J. L.; Allouche, E. N.,  
38 578 Corrosion of steel bars induced by accelerated carbonation in low and high calcium fly ash  
39 579 geopolymer concretes. *Constr. Build. Mater.* **2014**, *61*, 79-89. DOI  
40 580 10.1016/j.conbuildmat.2014.03.015  
41  
42  
43  
44 581 58. Mundra, S.; Criado, M.; Bernal, S. A.; Provis, J. L., Chloride-induced corrosion of  
45 582 steel rebars in simulated pore solutions of alkali-activated concretes. *Cem. Concr. Res.* **2017**,  
46 583 *100*, 385-397. DOI 10.1016/j.cemconres.2017.08.006  
47  
48  
49  
50 584  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60



585

586 **Graphical abstract: a chemically modified slag-based cement that retains**  
587 **its strength after carbon dioxide exposure.**

588