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DOI

[10.1016/j.cemconres.2018.11.011](https://doi.org/10.1016/j.cemconres.2018.11.011)

Publication date

2019

Document Version

Accepted author manuscript

Published in

Cement and Concrete Research

Citation (APA)

Nedeljković, M., Ghiassi, B., van der Laan, S., Li, Z., & Ye, G. (2019). Effect of curing conditions on the pore solution and carbonation resistance of alkali-activated fly ash and slag pastes. *Cement and Concrete Research*, 116, 146-158. <https://doi.org/10.1016/j.cemconres.2018.11.011>

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Effect of curing conditions on the pore solution and carbonation resistance of alkali-activated fly ash and slag pastes

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ABSTRACT

The effect of curing conditions (**sealed and unsealed**) on the pore solution composition and carbonation resistance of different binary alkali-activated fly ash (FA) and ground granulated blast furnace slag (GBFS) pastes is investigated in this study. **The studied mixtures were with FA/GBFS ratios** of 100:0, 70:30; 50:50, 30:70, 0:100. Ordinary Portland cement (OPC) and Cement III/B (70 wt.% of GBFS and 30 wt.% OPC) pastes with the same precursor content were also studied to provide a baseline for comparison. **Accelerated carbonation conditions (1% (v/v) CO₂, 60% RH for 500 days) were considered for evaluating the carbonation resistance of the pastes.**

38 The results show a substantial lower $[Na^+]$ in the pore solution of the unsealed cured
39 samples compared to the sealed cured samples. It is also found that unsealed curing of the
40 samples leads to a faster carbonation rate. Additionally, it is observed that the carbonation rate
41 decreases with increasing GBFS content independent of the curing conditions. The potential
42 risks with respect to carbonation of the pore solution are also identified and discussed.

43 **Keywords:** Alkali-activated fly ash/slag; Curing condition; Pore solution; Carbonation.

44

45 1. Introduction

46 Carbonation is one of the most harmful degradation processes that can significantly
47 affect the performance of reinforced Portland cement (OPC)-based concrete structures [1] and
48 for this reason, has been the subject of many studies in the literature [2-6]. Understanding this
49 degradation mechanism in alkali-activated materials (AAMs) that has received extensive
50 attention as a sustainable construction material is therefore of critical importance for their
51 standardization and use in practice [7].

52 In conventional OPC-based concrete, carbonation is the result of chemical reaction
53 between carbonic acid and cement hydration products that leads to precipitation of
54 carbonation products and decrease in the pH of the pore solution [8]. Carbonic acid is formed
55 in the pore solution by dissolution of gaseous CO_2 that diffuses from the environment into the
56 porous structure of the concrete. Carbonation, which is controlled by both diffusion and
57 chemical reaction, is dependent on several factors including relative humidity, tortuosity of
58 the paste, concentration of CO_2 in the environment and chemistry of the binder [9, 10].

59 Although the carbonation mechanism in AAMs is not yet fully understood, it is
60 expected to be different from that of OPC-based concrete. The fundamental differences in the
61 constituting phases and the physical structure of AAMs in comparison to OPC-based

62 materials is the main reason for such an expectation [11]. While the main reaction products in
63 OPC-based materials are $\text{Ca}(\text{OH})_2$ and C-S-H, different types of alkaline gel are formed in
64 AAMs, such as sodium aluminosilicate hydrate (N-A-S-H), calcium aluminosilicate hydrate
65 (C-A-S-H) and calcium sodium aluminosilicate hydrate (C-N-A-S-H) [12-14]. AAMs in
66 contrast to OPC-based concrete, do not contain $\text{Ca}(\text{OH})_2$ [15]. The absence of $\text{Ca}(\text{OH})_2$, that
67 acts as the main buffering compound in OPC-based concrete, leads to faster decalcification of
68 C-A-S-H/C-N-A-S-H gels and may account for the faster carbonation process in AAMs [16,
69 17].

70 It seems that carbonation in AAMs occurs in two main steps [18]: (1) Carbonation of
71 the pore solution leading to reduction of pH and precipitation of Na-rich carbonates; (2)
72 decalcification of Ca-rich phases and secondary products present in the system. This suggests
73 that the carbonation resistance of AAMs is not only a function of their binding capacity (or
74 the reactive CaO content) as reported for cement based materials [10], but also of the Na_2O
75 content consumed during the reaction of the precursors (e.g. FA and GBFS) [19].
76 Furthermore, the carbonation mechanism is strongly influenced by the type of the precursor
77 (FA, GBFS or metakaoline) [20-22], the nature and dosage of the alkaline activator used [23],
78 the exposure conditions [24] and the curing conditions, amongst others. While several recent
79 studies can be found in the literature investigating the effects of these parameters on the
80 carbonation resistance of AAMs, the role of curing conditions on the potential Na^+ loss and
81 carbonation resistance has not been reported yet.

82 The use of highly alkaline activators for reactions of the FA and GBFS provides a high
83 $[\text{Na}^+]$ leading to high pH levels in the pore solution of noncarbonated AAMs. It has been
84 shown that this ensures existence of sufficiently high $[\text{Na}^+]$ after natural and accelerated
85 carbonation in alkali-activated systems to prevent corrosion of reinforcement [19]. However,

86 it is not clear whether the susceptibility of AAMs to loss of Na⁺ ions prior to (or during) the
87 carbonation process can lead to significant decrease of pH or not [25-27].

88 The aim of this paper is to address these questions by investigating the effect of curing
89 conditions on the pore solution chemistry and carbonation resistance of alkali-activated
90 FA/GBFS pastes. Special attention is given to the Na⁺ loss in sealed and unsealed cured
91 specimens. Five mixtures with different FA/GBFS ratio are investigated. OPC (CEM I) and
92 CEM III/B pastes are considered to provide a baseline and to perform comparisons with the
93 studied alkali activated pastes.

94 2. Materials and methods

95 2.1 Materials and sample preparation

96 FA was supplied by VLIEGASUNIE BV and GBFS was supplied by ORCEM (the
97 Netherlands). CEM I 42.5 N and CEM III/B 42.5 N in compliance with Dutch standard
98 (NEN-EN 197-1:2011 en) were used as references. The chemical composition of raw
99 materials was determined with X-ray Fluorescence (XRF) (Table 1). XRF measurements were
100 done using Panalytical AXIOS Max Advanced XRF spectrometer. XRF analysis of raw
101 materials was performed with fused beads and lithium tetraborate/methaborate as a flux. XRF
102 bead analysis is not suitable for the analysis of sulfur. Therefore, sulphur (S) was determined
103 using Eltra Sulphur analyzer. Loss on ignition (LOI) was determined by LECO
104 Thermographic Analyser (TGA701). The negative LOI for GBFS (Table 1) was related to the
105 oxidation of sulfur rich species in the GBFS. It should be noted that the LOI was not corrected
106 in the XRF measurements. The average particle size of GBFS, d₅₀, was 19 μm, while for FA,
107 d₅₀ was 21 μm, as measured by the laser diffraction analyser.

108 **Table 1**

109 Chemical compositions of FA, GBFS, CEM I (42.5 N), CEM III-B measured with XRF [%].

	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	S	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	LOI
FA	56.8	23.8	4.8	1.5	7.2	0.3	0.8	1.6	1.2	0.5	1.2
GBFS	35.5	13.5	39.8	8.0	0.6	1.0	0.4	0.5	1.0	0.0	-1.3
CEM I	19.6	4.8	62.2	1.8	3.0	1.4	0.4	0.6	0.3	0.2	2.8
CEM III-B	30.0	11.0	45.0	7.0	1.3	1.9	0.4	0.5	0.9	0.6	0.1

110

111 Alkaline activator was prepared by mixing anhydrous pellets of sodium hydroxide
 112 with deionized water and commercial sodium silicate solution (27.5 wt.% SiO₂, 8.25 wt.%
 113 Na₂O). After mixing, activator liquid was kept under the laboratory conditions with the
 114 temperature around 20°C to cool down for 24 h prior to the paste mixing. The activator Na₂O
 115 concentration was 4.8 wt.% with respect to the mass of precursor (FA + GBFS). For each
 116 paste, the activator liquid to binder mass ratio was 0.5. The pastes were produced with the
 117 following FA/GBFS ratios of 100:0, 70:30, 50:50, 30:70, 0:100 wt.%, named S0, S30, S50,
 118 S70, S100, respectively (Table 2). Cement pastes were made with water-to-binder ratio 0.5.

119 **Table 2**

120 Mixture design for pastes with respect to 100 g of the binder.

Mixture	FA ^a	GBFS ^b	OPC ^c	m(Na ₂ O)/ m(binder)	SiO ₂ / Na ₂ O	water/ binder	activator liquid/ binder	Curing regime
S0	100	0	0	4.80	1.45	0.38	0.50	Unsealed/ Sealed
S30	70	30						
S50	50	50						
S70	30	70						
S100	0	100						
CEM III-B	0	70	30	-	-	0.50		
CEM I	0	0	100					

121 ^{a, b, c}weight percentage with respect to raw material (FA, GBFS, OPC) content (wt. %).

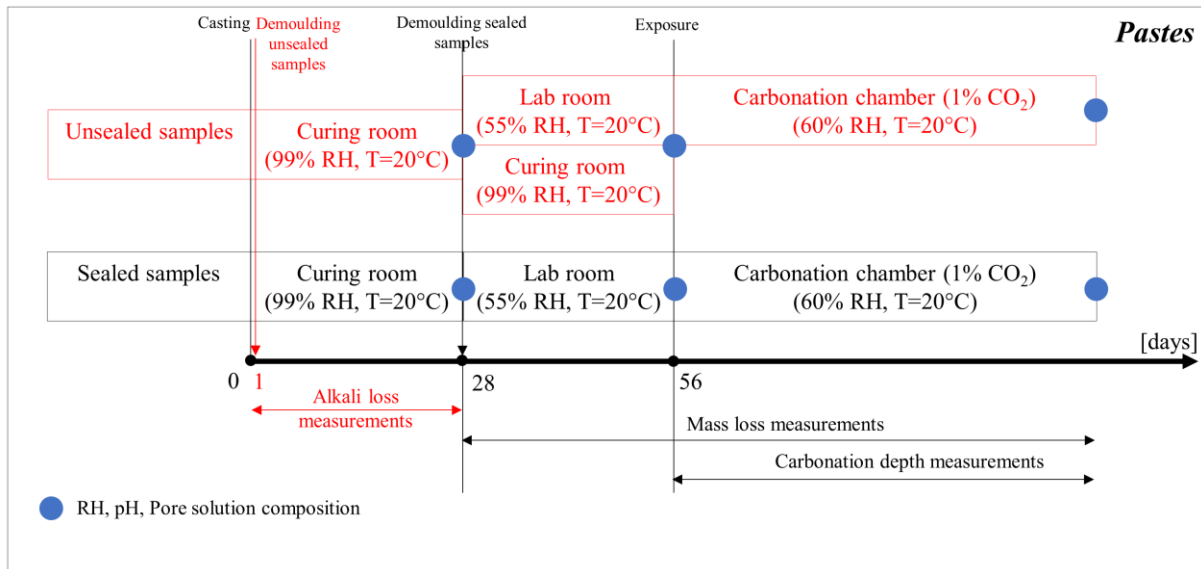
122 The precursors were dry-mixed for 2 minutes and then mixed with the activator. The
 123 pastes were cast in two types of cylindrical polyethylene jars, (A) with 35 mm diameter and 70

124 mm height, and (B) with 54 mm diameter and 100 mm height and vibrated for 15-30 s on a
125 vibrating table. The samples denoted as (A) were used for RH measurements pore solution
126 extraction and alkali loss measurements, while samples (B) were used for mass loss,
127 carbonation depth and pH measurements. The samples were stored in the closed jars (A, B)
128 for 24 h after casting. For unsealed cured conditions, samples were removed from the jars and
129 afterwards cured in a fog room at room temperature and a relative humidity (RH) of ~99%
130 RH (the atmosphere was normal air with 400 ppm of CO₂ and the air was internally
131 circulated, however, when opening the curing room, air with CO₂ is expected to enter the fog
132 room) for 28 days. For sealed samples, these were kept in the jars in the curing room where
133 unsealed samples were also cured.

134 2.2 Test programme

135 An overview is shown in the Fig. 1 of the test programme followed to investigate the
136 effect of curing conditions and accelerated carbonation on the alkali-activated FA/GBFS
137 pastes. First mass loss, internal RH, pore solution composition and pH are studied both for
138 curing under sealed and unsealed conditions. Additionally, alkali loss was monitored for
139 unsealed cured samples during the first 28 days of curing. The sealed samples were unsealed
140 after 28 days of curing when all the samples were placed in the laboratory conditions at 55-
141 60% RH (0.04% v/v CO₂, 20°C) for additional 28 days (preconditioning of the samples prior
142 to carbonation). This preconditioning was intended to equilibrate the internal RH of the
143 samples with the environment before performing the accelerated carbonation tests. For
144 unsealed samples, one set was left in the curing room for an additional 28 days, to provide
145 insight into the further alkali loss after first 28 days of curing.

146 During carbonation exposure, the carbonation depth was monitored in both sealed and
147 unsealed cured samples.



148

149

Fig. 1. Schematic representation of the test programme.

150

151 2.2.1 RH measurements

152

153 Free water in the pore structure of the pastes is critical for carbonation progress. In

154 order to ensure that the internal relative humidity of the pastes is in equilibrium with RH of

155 the carbonation chamber, the internal RH of the pastes was measured after 1 day (before

156 demoulding of the samples), after 28 days of curing and after 28 days of preconditioning (a

157 total of 56 days). The procedure for internal RH measurements follows Huang et al. [28]. The

158 internal RH of bulk pastes (A) was measured by Rotronic HygroLab C1 equipped with two

159 HC2-AW RH station probes with an accuracy of ± 1 % RH. The RH probes were calibrated

160 using saturated salt solutions with known constant RH in the range of 65-95%. The samples

161 were cut in thin slices of less than 7 mm, so in the sample holder there were a few slices of

162 one sample. The sample slices were then put in two plastic containers in the measuring

163 chambers. Samples and atmosphere equilibrated in 3-5 hours. The measured RH represents

164 the average of the internal RH and it is not related to RH of a specific depth of the samples.

165

166 2.2.2 Mass loss measurements

167

168 Mass loss measurements were used to assure that preconditioning period of 28 days is
169 sufficient prior exposure of samples to accelerated carbonation. The mass loss of the sealed
170 and unsealed pastes after 28 days of curing was monitored in the laboratory conditions (55%
171 RH, 20 °C) until constant mass was reached. The mass of samples was measured since the
172 samples were removed from the curing room. It was observed that at the age of 56 days the
173 difference between two measurements was less than 0.01 g. Based on this observation, the
174 samples were preconditioned for 28 days before carbonation exposure (curing of 28 days and
175 preconditioning of 28 days), as indicated in Fig. 1. The evaporable water in the pastes was
176 also determined (at specific periods) by measuring the weight loss per gram of the samples at
177 105°C in an oven (Jouan oven Type E455 EL), until reaching a constant weight.

178

179 2.2.3 Pore solution composition and pH measurements

180

181 Procedure for pore solution extraction from alkali-activated FA/GBFS pastes is adopted
182 from [29]. The pore solutions were pressed out from the pastes (type A sample size with 35
183 mm diameter and 70 mm height) with a high-pressure apparatus MacBen-type, with an oil-
184 hydraulic end-load capacity of 5000 kN and a cylinder assembly with an inner diameter of 34
185 mm and a height of 115 mm fitting the size of the paste cylinders (A). Pressures of up to 750
186 MPa were used to extract the pore fluid. The fluid was extracted through a drain channel and
187 collected in a syringe with almost no exposure to the atmosphere. Around 0.5 to 5 ml of pore
188 solution could be collected for each sample depending on the type of the paste and the curing
189 age. The pressed-out pore solutions were filtered using Whatman 41 filter paper and half of
190 each solution was diluted using nitric acid (0.2 vol.%). Inductively coupled plasma optical
191 emission spectrometry (ICP-OES) was used for chemical analysis of the pore solution

192 **composition.** Chemical analyses of diluted solutions were carried out with a Perkin Elmer
193 Optima 5300 DV apparatus.

194 The pH was measured on the non-diluted solutions. The non-diluted solutions of the
195 samples cured for 28 days and 56 days were left for measurement of $[\text{OH}^-]$ by titration against
196 HCl acid. While pore fluid extraction from the original samples was successful, direct
197 extraction from carbonated samples was not possible due to both the low relative humidity
198 used during the carbonation process and the small amount of sample material. Therefore, the
199 pH measurements were carried out on simulated pore solutions similar to [30], by
200 equilibrating 1 g of powdered paste (bulk pastes were crushed and ground into a powder) with
201 10 ml of de-ionized water during 15 minutes at ambient temperature while stirring with a
202 magnetic bar. Subsequently, the pH of the suspension was measured by pH meter 827
203 Metrohm. **The powders were obtained from the outer surface of the samples within a**
204 **thickness of 1 mm. These simulated pore solutions were used as a substitute for pressed-out**
205 **fluids to compare non-carbonated samples with 500 days curing (as reference) with samples**
206 **carbonated for 500 days.**

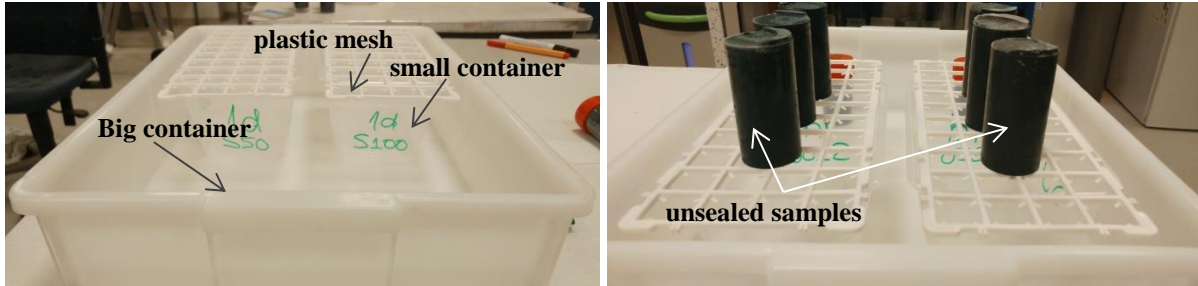
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208 2.2.4 Alkali loss measurements

209

210 It was noticed from measurements of the pore solution composition that unsealed
211 curing is associated with a leaching process induced by the RH of curing room in which
212 mainly Na^+ loss from the paste body occurs. A common curing set-up was used for alkali loss
213 measurements to confirm Na^+ loss. The test set-up is shown in Fig. 2. The specimens (sealed
214 and unsealed) after 1 day of casting, were placed in the curing room with 99% RH and 20°C.
215 Moisture condensed on the surface of the specimens was collected in plastic containers that
216 were placed under the specimens. After 1, 4, 7, 21, 28 days, the liquid from the plastic
217 containers was collected to analyse $[\text{Na}^+]$ in the leached solutions. The collected liquid was

218 filtered using Whatman 41 filter paper. Afterwards, the liquid was diluted using nitric acid
219 (0.2 vol.%). Chemical analyses of the diluted liquids were carried out with a Perkin Elmer
220 Optima 5300 DV apparatus.



221

222 **Fig. 2.** Set up for alkali loss measurements.

223

224 2.2.5 Accelerated carbonation conditions and carbonation depth measurements

225

226 **Accelerated carbonation started 56 days after curing and preconditioning, in a CO₂**
227 **atmosphere of 1% v/v at 60% RH and at 20°C.** The CO₂ of 1% v/v was chosen since it was
228 reported by Bernal et al. [20] that conducting accelerated carbonation using CO₂
229 concentrations beyond CO₂~1% v/v will not accurately replicate the carbonation mechanisms
230 observed in service. The carbonation depth was measured with phenolphthalein, according to
231 the standard EN 13295:2004. Carbonation depths of the cylindrical pastes (B) were measured
232 after 1, 7, 14, 28, 56, 90, 180, 270, 365, 500 days of CO₂ exposure. The cylinders were split
233 and the fresh surface was sprayed with a 1 wt. % phenolphthalein solution (comprising 1 g of
234 phenolphthalein in a solution of 70 ml ethanol and 30 ml demineralized water). The recorded
235 carbonation depths are the average of measurements at 10 locations on the sample.

236

237 2.2.6 ESEM-EDX

238

239 **Investigation of the morphology and element composition of the deposits found on the**
240 **surface of the unsealed cured samples and in the small plastic containers (Fig. 2) was done**

241 with the Philips-XL30-ESEM microscope, equipped with NSS.3.3. The deposit was collected
242 from the sample surface with a brush, while the liquid drop of the deposit was collected from
243 the small plastic container. For scanning electron microscope/energy-dispersive X-ray (SEM-
244 EDX) analysis, deposits were placed onto carbon-coated sticky stubs and directly observed
245 under the ESEM-BSE mode.

246

247

248 3. Results and discussions

249 3.1 Effect of the curing conditions

250 3.1.1 Mass loss and internal RH

251

252 The changes of the mass of the specimens with time are presented in Fig. 3 and Fig. 4.
253 The total mass percentage of water loss in the pastes due to drying after 28 days storage in the
254 laboratory conditions (55% RH and 20°C) is presented in Table 3. It proves that in all samples
255 a fluid phase is present and that RH is not buffered solely by solid phases when starting
256 carbonation.

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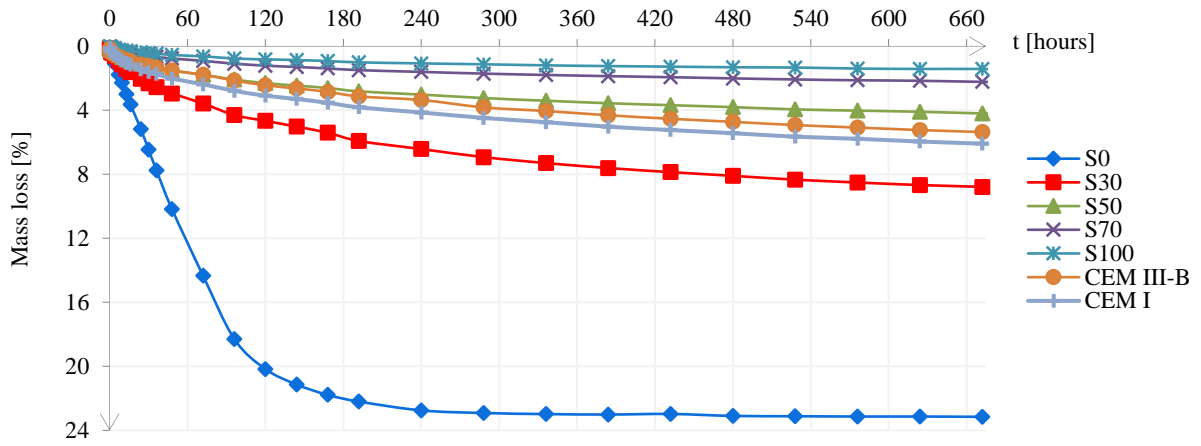
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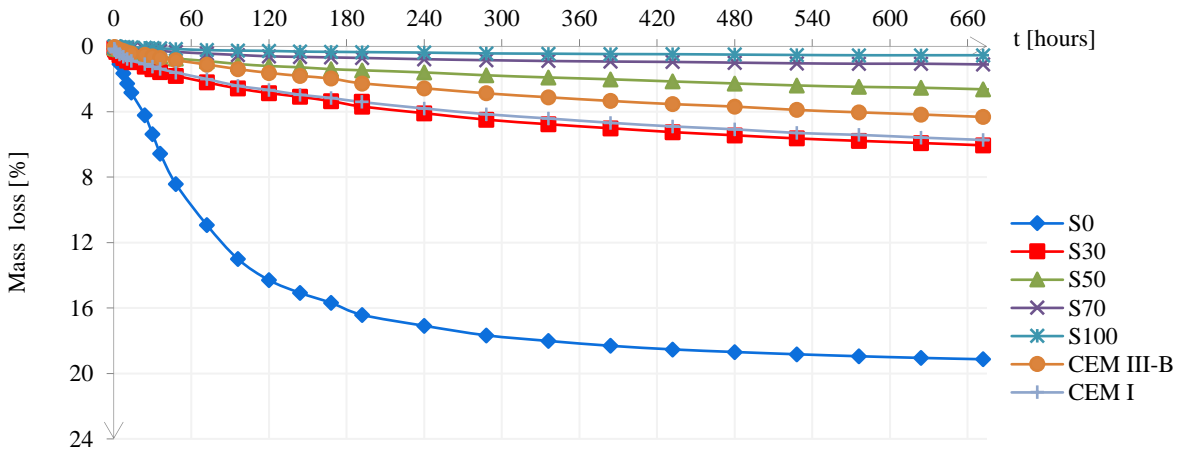
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270 **Fig. 3.** Unsealed samples first 28 days; mass loss measured from 28 days.

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277 **Fig. 4.** Sealed samples first 28 days; mass loss measured from 28 days.

278 **Table 3**

279 Water loss (in mass percentage) and internal RH of the pastes*.

	Sample mass [g]		Water loss [wt.%]						Internal RH [%]				
	At age of 28 days		Stored in lab RH 55% conditions from age of 28 d to 56 d		Heating at 105°C (at 56d)		Total water loss		1d**	28d		56d	
			sealed	unsealed	sealed	unsealed	sealed	unsealed	sealed	unsealed	sealed	unsealed	sealed
S0	349.5	359.8	19.13	23.15	5.05	3.08	24.18	26.23	> 95.00	> 95.00	> 95.00	64.1	64.3
S30	376.6	379.4	6.05	8.78	14.45	13.87	20.50	22.65	> 95.00	> 95.00	> 95.00	64.6	65.0
S50	382.0	381.7	2.63	4.20	16.90	17.00	19.53	21.20	91.88	90.30	94.00	64.1	65.0
S70	401.0	397.4	1.10	2.22	17.81	17.80	18.91	20.02	88.12	80.80	80.00	63.8	64.0
S100	413.0	413.9	0.55	1.42	16.73	17.12	17.28	18.54	87.07	71.50	73.00	62.3	62.0
CEM III/B	365.0	358.2	4.32	5.36	19.96	20.39	24.28	25.75	> 95.00	> 95.00	> 95.00	78.9	80.0
CEM I	353.0	342.9	5.72	6.08	22.00	22.10	27.72	28.18	> 95.00	> 95.00	> 95.00	70.4	73.0

280 *‘Sealed’ are the samples that were cured in sealed conditions first 28 days and then demoulded and exposed to lab conditions until 56 days. ‘Unsealed’ are the samples that
 281 were cured in 20 °C, ~99 % RH conditions during the first 28 days and further exposed to lab conditions until 56 days.

282 **The 1d internal RH presents the time zero when the samples were removed from moulds to curing room (all samples were kept in moulds for 1 day before curing in the fog
 283 room). The RH of the activation solution (NaOH+WG) before mixing with raw FA and GBFS was 92.03%.

284 In general, the amount of evaporable water for the unsealed cured samples are higher
285 compared to the sealed. The amount of evaporable water between conditions of 99% RH and
286 28 days curing and subsequent 55% RH exposure until 56 days is the highest in paste S0 and
287 the lowest in paste S100. In alkali-activated FA materials, a much higher Na₂O concentration
288 and curing temperatures (> 40°C) are required for a complete dissolution of FA [31]. In the
289 present study, due to the low Na₂O concentration of the alkaline activator and the applied
290 curing conditions (ambient temperature) paste S0 has a limited degree of reaction which is
291 supported by the low strength development observed in [32]. This low reaction degree implies
292 the existence of physical water in the pores as experimentally measured here, see Fig. 3 and
293 Fig. 4. On the other hand, based on the measurements of the evaporable water content at
294 105°C, it can be seen that with increasing GBFS content more evaporable water is measured
295 at 105°C, than at 55% RH. This suggests that GBFS-rich pastes have more chemically bound
296 water than FA-rich pastes. Another effect that can be observed is that with increasing GBFS
297 the total free water (sum of evaporated at 55% RH + mass loss at 105°C) decreases, implying
298 that some water must become structurally bound in the samples equivalent to self-dessication.

299 The mechanisms affecting the transport of physical water in unsealed cured samples
300 are illustrated in Fig. 5a. The loss of alkalis in the case of unsealed samples exposed to 99%
301 RH is due to several counter-affecting phenomena (Fig.5b). The RH of the activation solution
302 (NaOH+WG) before mixing with raw FA and GBFS was 92.03%, while the RH of the pastes
303 S30, S50, S70 and S100 at 1 day (when 99% RH curing initiated) was 95.86%, 91.88%,
304 88.12%, 86.98%, respectively (see Table 3). This difference in the RH of the environment and
305 the specimen, causes a capillary flow from the surface to the interior of the samples and
306 therefore an inward movement of the ions (advection). Meanwhile, condensation of water on
307 the surface of the samples leads to dilution of the ions at the surface compared to the interior
308 of the specimens. This causes a diffusive movement of ions from the interior towards the

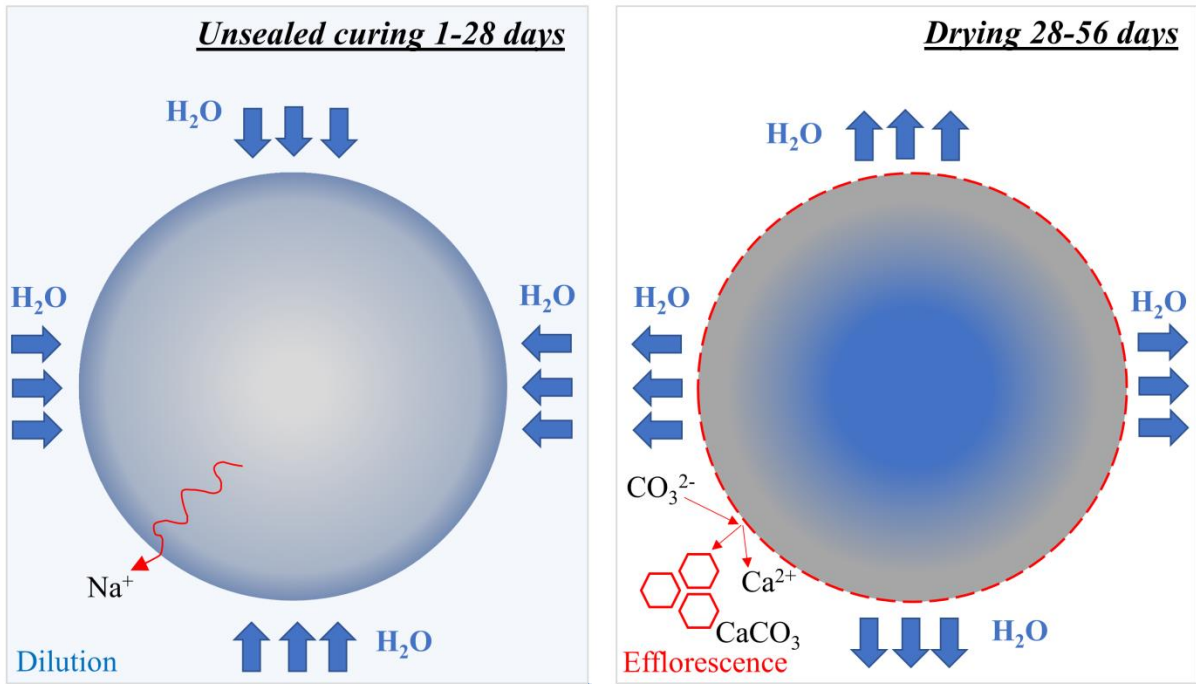
309 surface of the samples. There is, therefore, a clear competition between both phenomena.
310 Based on the observed $[\text{Na}^+]$ difference in the pore solution in sealed and unsealed curing
311 conditions (see Table 4), the second mechanism is predominant in the studied samples. Both
312 advection and diffusion are governed by the microstructure of the paste and, for that reason,
313 the alkali loss is different between the studied alkali activated pastes (see Fig. 9).

314 On the other hand, when samples are moved from the curing room, subsequent drying
315 of the surface causes efflorescence (see Fig. 5a, drying 28-56 days). The product of
316 efflorescence is calcite as will be shown in Fig. 8a. Calcite was formed already in the curing
317 room on the wet outer surface of the samples. In the high pH fluid, CO_2 will be present as
318 CO_3^{2-} and together with Ca^{2+} it forms calcite. The calcium carbonate efflorescence is
319 promoted even at smaller amounts of alkali dissolved in the aqueous film such as in cement
320 based pastes [33], compared to alkali activated pastes.

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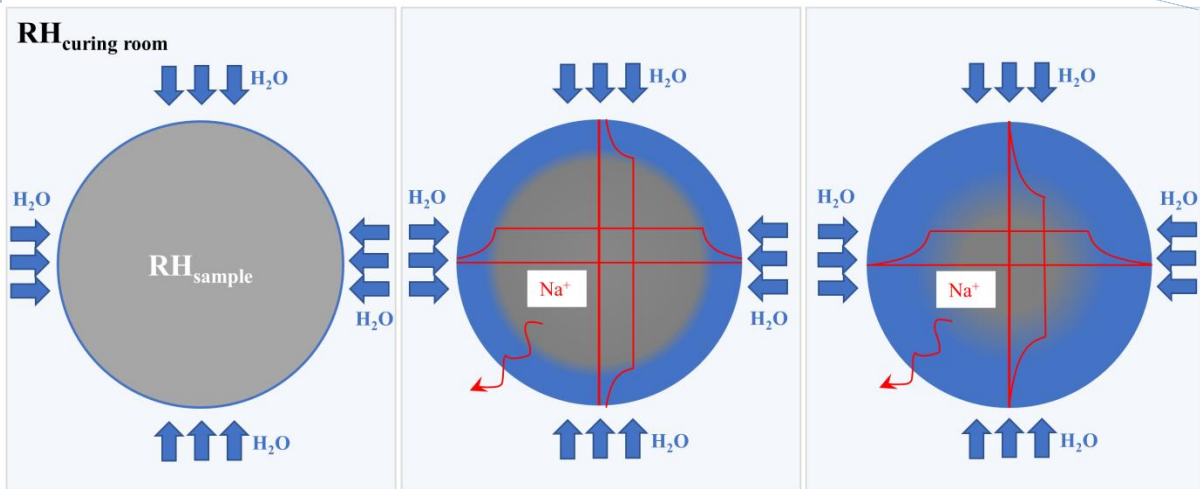


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(a) Illustration of the direction of water transports during the unsealed curing (1-28 days) and drying of the pastes (28-56 days).



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(b) Illustration of the boundary conditions during the water transport and Na^+ loss in the unsealed curing conditions of the pastes (1-28 days):

left: day 1, demoulding of the samples and subsequent exposure of the samples to 99% RH;

middle: advective movement of Na^+ by dilution of the pore solution at the surface of the samples followed by diffusive movement of Na^+ ;

right: diffusive movement of Na^+ from the interior towards the surface of the samples.

334

335

336

Fig. 5. (a) Illustration of the water transport during the unsealed curing (1-28 days) and drying of the pastes (28-56 days); (b) illustration of the boundary conditions during the water transfer and Na^+ loss in the unsealed curing conditions of the pastes (1-28 days).

337 The internal RH of the pastes was also measured at the age of 28 days (before storage
338 in the laboratory conditions) and at the age of 56 days (after 28 days of storage in the
339 laboratory conditions) as shown in Table 3. The RH of the unsealed samples is generally
340 higher than the equivalent sealed samples, which is consistent with the pore fluids being more
341 diluted in the unsealed samples, thus having a higher water activity. The results, presented in
342 Table 3, show that the internal RH of the pastes at 28 days decreases with increment of GBFS
343 content (from paste S0 to S100). This phenomenon can be attributed to the self-desiccation in
344 these mixtures [34] and it has a similar effect on the sealed and unsealed samples.

345 The RH of the samples after 56 days shows that the samples have not reached the
346 equilibrium condition with the environment yet. The internal RH of alkali-activated pastes is
347 around 62-65% RH at this age. As the accelerated carbonation tests are performed at 60% RH,
348 it is expected that RH of the samples was likely equilibrated with RH of exposure site in a
349 short time after the start of the experiment. The pastes CEM I and CEM III/B showed a higher
350 internal RH compared to alkali-activated pastes showing that the drying is slower in these
351 materials. The internal RH of CEM I paste with water-to-cement ratio 0.5 at 28 days is in
352 agreement with the literature [35].

353

354 3.1.2 pH and composition of the pore solution

355

356 The pore solution analysis was performed on both groups (sealed and unsealed) of
357 samples after 28 and 56 days of curing. This analysis enabled the quantification of the
358 concentration of the main ions (Na^+ , K^+ , Ca^{2+} , S^{2-}) in the pore solution and measurement of
359 pH. Results of pH and composition of the pore solution are presented in Table 4 and Table 5.

360

361 **Table 4**

362 pH values and main element composition of pastes pore solutions analyzed with ICP-OES (28
 363 days). **The pore solutions were extracted with high pressure method.**

		pH	[Na]	[K]	[Ca]	[S]	Porosity
Curing room (99% RH)		[-]	[mmol/L]	[mmol/L]	[mmol/L]	[mmol/L]	[%] ^[36]
S0	Sealed	13.40	1336	20	21.73	298	
	Unsealed	13.02	101	4	33.08	< 1.5	43.71
S30	Sealed	13.45	1004	23	19.40	375	
	Unsealed	13.16	150	3	8.63	51	26.04
S50	Sealed	13.70	1078	26	8.48	292	
	Unsealed	13.30	211	4	3.35	79	9.4
S70	Sealed	13.80	1115	27	23.10	378	
	Unsealed	13.40	326	7	10.23	172	6.54
S100	Sealed	14.00	1556	36	29.50	573	
	Unsealed	13.60	551	11	19.63	326	3.57
CEM III B	Sealed	13.08	61	58	44.08	-	
	Unsealed	13.00	56	45	12.80	5	48.87
CEM I	Sealed	13.62	193	230	39.28	-	
	Unsealed	13.28	105	85	4.75	< 1.5	46.48

364

365 **Table 5**

366 pH values and main element composition of pastes pore solutions analyzed with ICP-OES (56
 367 days). **The pore solutions were extracted with high pressure method.**

		pH	[Na]	[K]	[Ca]	[S]
		[-]	[mmol/L]	[mmol/L]	[mmol/L]	[mmol/L]
S0	Sealed*					
	Unsealed L**					
	Unsealed C***	12.40	29	1	3.80	
S30	Sealed*					
	Unsealed L**					
	Unsealed C***	13.00	106	2	3.15	
S50	Sealed*	13.72	1233	18	10.85	
	Unsealed L**	13.58	424	6	54.68	
	Unsealed C***	13.25	187	4	3.45	
S70	Sealed*	13.80	1363	32	29.55	0.42
	Unsealed L**	13.60	426	6	3.50	0.26
	Unsealed C***	13.34	268	6	5.58	
S100	Sealed*	14.00	1544	36	5.73	0.55
	Unsealed L**	13.60	557	10	12.88	0.32
	Unsealed C***	13.53	463	10	2.65	
CEM III	Sealed*					

B	Unsealed L**					
	Unsealed C***	13.05	59	53	1.95	
CEM I	Sealed*					
	Unsealed L**					
	Unsealed C***	13.29	116.13	79	15.58	

368 *Samples that were sealed cured for 28 days, demoulded at 28 days and further kept in
369 unsealed laboratory conditions (55 % RH) until 56 days.

370 **Samples that were unsealed cured for 28 days, and further kept in unsealed laboratory
371 conditions (55 % RH) until 56 days.

372 ***Samples that were unsealed cured for 28 days, and further kept in unsealed curing
373 conditions (99 % RH) until 56 days.

374

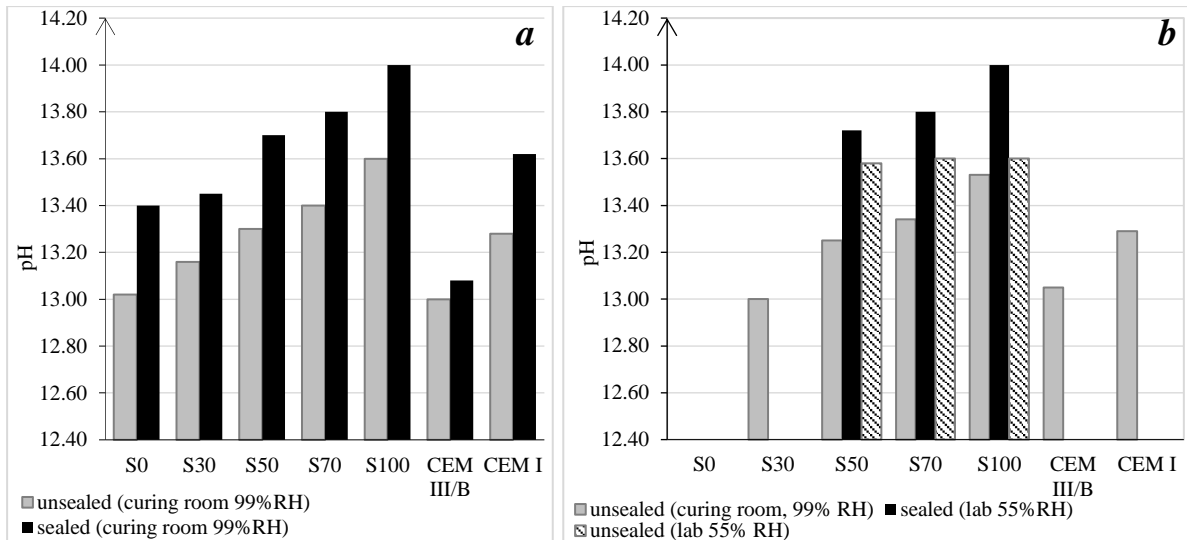
375 It can be observed that the pH of all sealed alkali-activated pastes is in the range of
376 13.4 to 14.0 at 28 days of curing, as expected. This value is lower in the unsealed equivalent
377 pastes (but still higher than 13.0), which is due to Na-hydroxide loss from these specimens.
378 Additionally, no specific change of pH is observed at 56 days of curing compared to 28 days
379 (Fig. 6). A similar effect is also observed in CEM I paste. The pH in the sealed samples is
380 generally higher than in unsealed pastes. This difference is smaller in CEM III/B pastes.

381 The $[\text{Na}^+]$ in the alkaline activator before mixing with raw materials was 4026
382 mmol/L. After 28 days of curing in sealed conditions, it can be seen that this value, in pastes
383 (S0-S100), is reduced to the range of 1004 mmol/L to 1556 mmol/L (Fig. 7 left). It is clear
384 that a part of Na^+ is taken up during the formation of reaction products, while the other part of
385 Na^+ is present in the pore solution (or leached in the unsealed cured samples).

386 The effect of FA/GBFS ratio on the $[\text{Na}^+]$ in the pore solution is not clear at 28 days.
387 The pastes S0 (100% FA) and S100 (100% GBFS) have the highest $[\text{Na}^+]$, while in pastes
388 S30, S50 and S70 the $[\text{Na}^+]$ increases with increasing the content of GBFS. On the other hand,
389 the $[\text{K}^+]$ always increases with increasing GBFS content (see Table 4). A relatively high $[\text{S}^{2-}]$
390 is found in the pore solutions with no specific correlation with the FA/GBFS ratio. Compared
391 to pastes CEM I and CEM III/B, the pore solution in alkali-activated pastes contains a
392 significantly higher $[\text{Na}^+]$, but a comparable $[\text{K}^+]$.

393 In contrast to CEM I and CEM III/B pastes, the $[\text{Na}^+]$ of pore solutions of unsealed
394 alkali activated pastes is still decreasing in all the pastes until 56 days in the curing room
395 (Table 5). This decrease is higher in pastes with a higher percentage of FA
396 (S0>S30>S50>S70>S100). This is in accordance with the differences in porosity of these
397 specimens measured at 28 days with mercury intrusion porosimetry (Table 4). It can be also
398 observed that the $[\text{Na}^+]$ of the pore solutions of unsealed samples in laboratory conditions is
399 higher than in the unsealed samples in curing room (see Fig. 7b). This was expected, as the
400 high relative humidity in the curing room promotes the loss of Na^+ in these specimens.

401 A comparison between $[\text{Na}^+]$, $[\text{K}^+]$, $[\text{Ca}^{2+}]$ and $[\text{S}^{2-}]$ in all samples clearly shows a
402 significant effect of the sealed and unsealed curing on the pore solution chemistry. A
403 significant drop in ion concentration can be observed in the pore solution in the unsealed
404 pastes. Fig. 7 shows the difference between $[\text{Na}^+]$ in these specimens at 28 days and 56 days,
405 respectively. It can be seen that these values are significantly lower in unsealed alkali-
406 activated pastes, but still remain at a higher level compared to CEM I and CEM III/B pastes.
407 The effect of loss on the $[\text{Na}^+]$ in OPC-based pastes is also significant, but seems negligible in
408 CEM III/B pastes. Alkali activated pastes, in direct contact with water during unsealed curing,
409 show Na^+ leaching. There is, therefore, a competition between the Na^+ consumption for the
410 reaction of FA and GBFS and the Na^+ loss due to leaching.

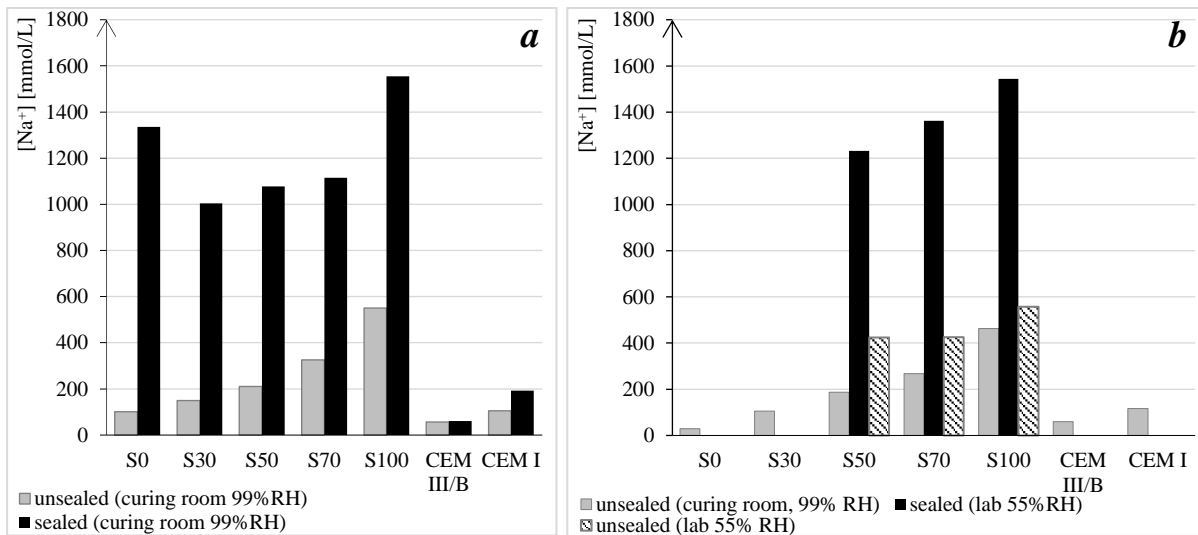


411

412

Fig. 6. The effect of sealing on the pH in the pore solution of the pastes at 28 days (a) and 56 days (b).

413



414

415

Fig. 7. The effect of sealing on the [Na⁺] in the pore solution of the pastes at 28 days (a) and 56 days (b).

416

417

418 3.1.3 Alkali loss

419

The alkali content in the pore solution can vary depending on the type of the curing conditions as shown in Section 3.1.2. Significant alkali loss was observed for unsealed cured samples. The mechanism for alkali loss was explained in Section 3.1.1. **The main role of the alkalis is to provide the right environment for dissolution of the FA and GBFS. In addition, the alkalis content in the pore solution of AAMs is highly important as they are the main**

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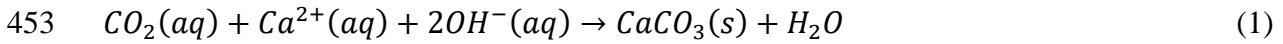
424 buffer for alkalinity during carbonation. Beside alkalis (Na), calcium ions may also contribute
425 to maintaining a high pH of the pore solution. This is supported by the authors' previous
426 study [37], where it was shown that not all the CaO was consumed by carbonation of studied
427 alkali activated pastes. This implies that, after NaOH carbonation, the remaining CaO can act
428 as a buffering agent for the pH of the pore solution.

429 Beside alkali loss, the efflorescence occurred in all samples cured in unsealed
430 conditions, except for pastes CEM I, CEM III/B and S0 as was observed when they were
431 moved from the fog room to the laboratory environment (55-60% RH). Although soluble
432 silicate and GBFS addition are found beneficial in reducing the efflorescence degree in
433 AAMs, they have limited influence on the overall efflorescence potential, as they appear to
434 have a delaying rather than mitigating effect [38]. The coexistence of water with water-
435 soluble salts and exposure to moisture gradients or wet/dry cycles are main conditions for
436 efflorescence. Evaporation of the aqueous salt solution may occur on the surface or in regions
437 near the surface when a moisture gradient between the ambient atmosphere and the material
438 exists. This resulted in the appearance of efflorescence on the surface of the unsealed cured
439 specimens (Fig. 8a). The efflorescence powder was collected carefully from the sample's
440 surfaces for further chemical analysis (Fig. 8a).

441 SEM-EDX analysis showed that the product of efflorescence was calcite (CaCO_3),
442 with the size of about 10-20 μm (Fig. 8b). Similar morphology was also observed in the study
443 by García-Carmona et al. [39], where the calcite particles were obtained by carbonation of
444 slaked lime in a semicontinuous process. The CaCO_3 formation in this study resulted from
445 $\text{Ca}^{2+}\text{OH}^-$ carbonation when the CO_2 and H_2O are simultaneously present and when the
446 solubility of calcite is exceeded. The $\text{Ca}^{2+}\text{OH}^-$ ion pair from solution is transported towards
447 the surface of the hardened paste where it reacts away to carbonate at the cylinder surface (see
448 Fig. 5). Since the precipitation takes Ca^{2+} out of solution, it is replenished by diffusion

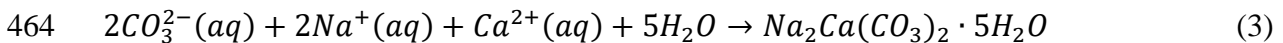
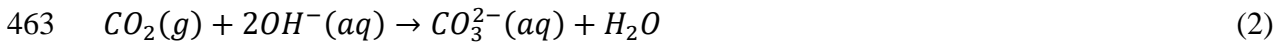
449 through the fluid and re-equilibration (Ca-release) from the gel. The final result of the several
450 steps through which the carbonates are formed can be described by the following reaction
451 similar to [40]:

452

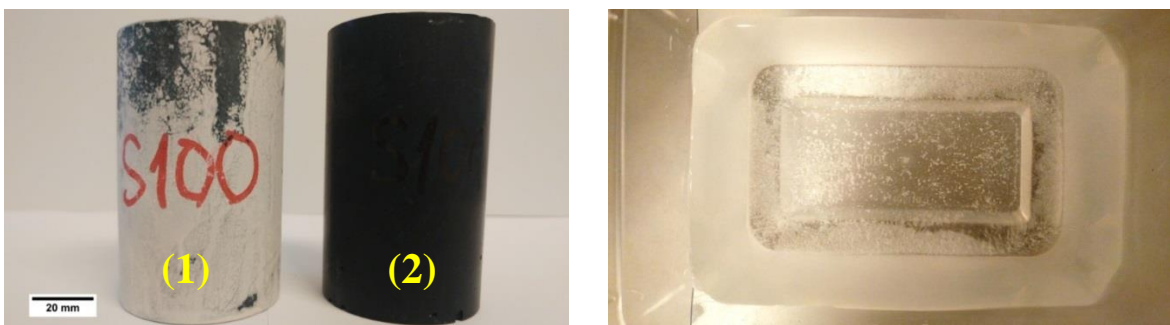


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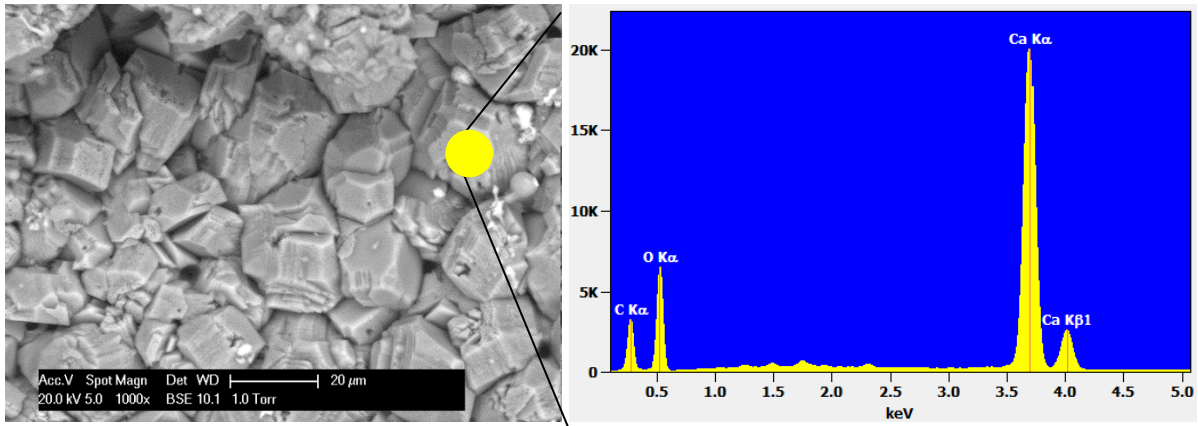
455 Meanwhile, the deposits from the plastic container in which the moisture from the
456 surface of the specimen S100 was collected after 1 day of unsealed curing, were also
457 analyzed. The carbon together with oxygen, sodium, calcium and traces of aluminium, silicon,
458 sulfur and potassium were detected as demonstrated by the EDX spectrum (Fig. 8c). The
459 anhedral crystals (Fig. 8c) are identified as gaylussite ($\text{Na}_2\text{Ca}(\text{CO}_3)_2 \cdot 5\text{H}_2\text{O}$) because they are
460 formed mostly of Na and Ca (EDX spectrum, Fig. 8c), similar to the gaylussite identification
461 by Jones et al. [41]. The mechanism of the Na, Ca-carbonate formation can be described by
462 the following reactions:



465

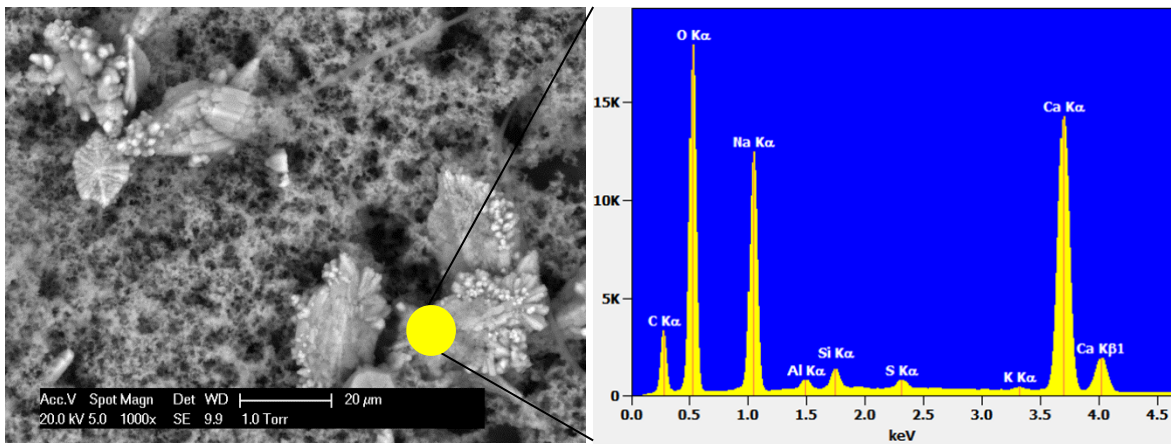


466 **Fig. 8a.** Pastes S100 at 56 days (left, (1)-unsealed cured sample, (2)-sealed cured sample), the
467 plastic container in which the fluid, condensed on the surface of the specimen S100, was
468 collected after 4 days of unsealed curing (right).

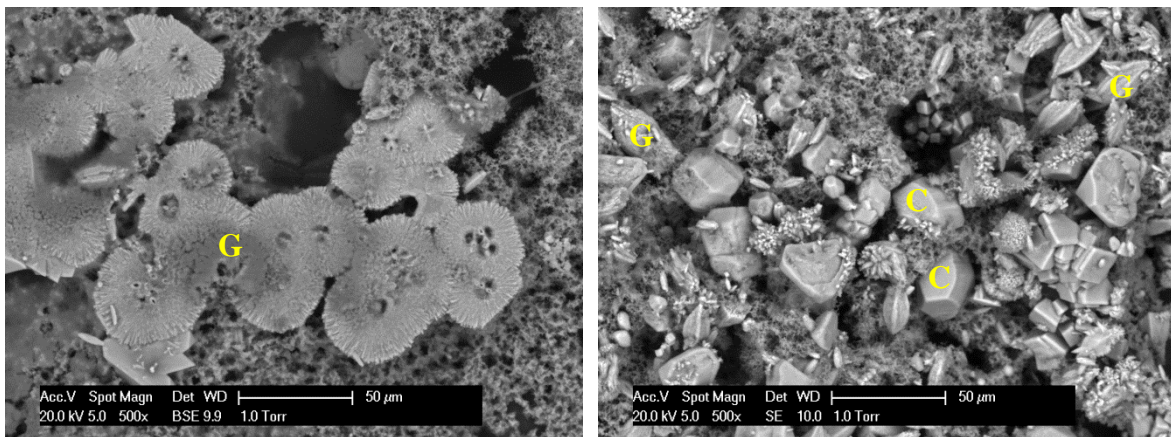


469

470 **Fig. 8b.** ESEM-BSE image and EDX spectrum of the deposit from the surface of the cylindric
 471 sample labelled as (1) shown in Fig. 8a.



472

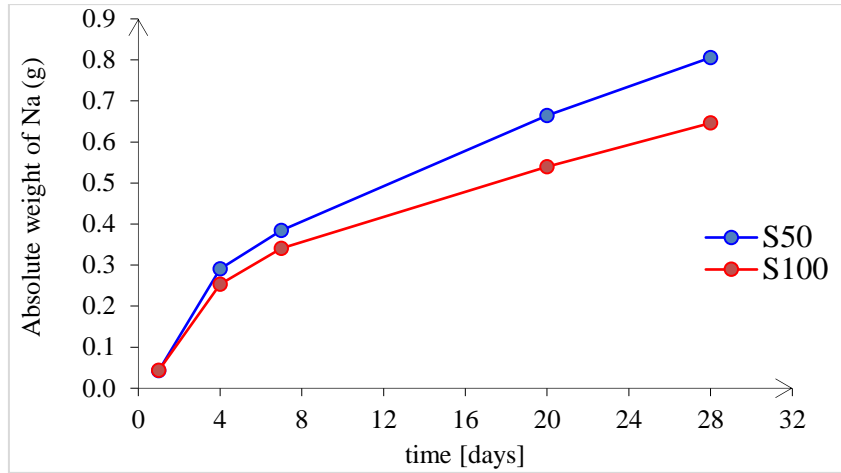


473

474 **Fig. 8c.** ESEM-BSE images and EDX spectrum of the deposit from the plastic container
 475 shown in Fig. 8a (Gaylussite-G, Calcite-C).

476 The ICP-OES results for Na⁺ from alkali loss experiments of the pastes S50 and S100
477 are presented in Fig. 9. It should be noted that this figure shows the cumulative amount of the
478 Na⁺ in the solutions collected in the plastic containers and for each stage the new measured
479 absolute amount of Na was added to the previous. The containers were removed for the Na⁺
480 measurement and a new empty container was placed for the collection of the fluid in the next
481 time segment to avoid saturation of the solutions with the solids precipitating in the containers
482 as shown in Fig. 8a, c. The results clearly show the continuous loss of Na⁺ from the samples
483 with time. It seems that the highest amount of alkali loss occurred between 7 and 28 days. The
484 leached Na amount is lower in specimen with higher GBFS content (Fig. 9). The higher alkali
485 loss in pastes S50 compared to pastes S100, is due to a more porous microstructure of paste
486 S50 compared to paste S100 as shown in Table 4, column 7. This facilitates the Na-leaching
487 process. Water from the curing atmosphere can more readily enter the gel and become self-
488 expelled in paste S50 compared to paste S100. The absolute mass of leached Na⁺ was
489 measured from the total solution volume which was collected in the plastic container during
490 28 days of unsealed curing of the samples S50 and S100. It is found that 0.8 g and 0.65 g of
491 Na⁺ was leached from the samples S50 and S100, respectively. The absolute amount of Na
492 which was initially used for the activation was 4.62 g. This implies that 17.3 % and 14 % of
493 this initial Na amount, was leached from the samples S50 and S100, respectively.

494 It should be noted that the ICP-OES analysis enabled the quantification of [Na⁺] in
495 solution but not of the [Na⁺] which already reacted with carbonate ions forming a solid during
496 alkali loss as found from SEM-EDX analysis (Fig. 8c). This implies that a higher amount of
497 Na was expelled than was measured in the experiments.



498

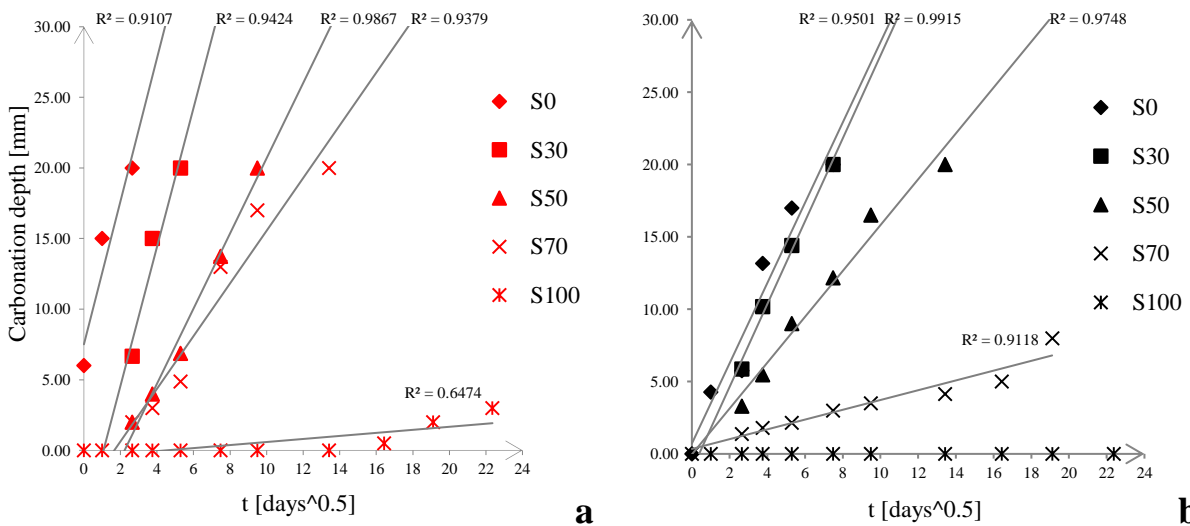
499 **Fig. 9.** Cumulative Na leached from the unsealed pastes (S50 and S100) during 28 days of
 500 curing in 99% RH.

501

502 **3.2 Effect of accelerated carbonation**

503 3.2.1 Carbonation depth

504 The carbonation depths were measured for both sealed and unsealed cured samples
 505 and the results are presented in Fig. 10.



506

507 **Fig. 10.** Carbonation rate for the unsealed cured samples (a), and for the sealed cured samples
 508 (b). R^2 is the correlation coefficient from the least-squares linear fits.

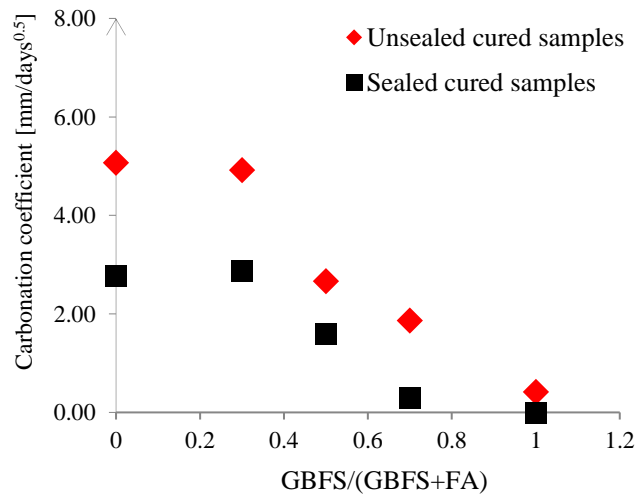
509 Carbonation was observed in the pastes S0, S30, S50 even after 1 day of exposure. It
510 can be seen that in general, the propagation rate of carbonation front is faster in the unsealed
511 cured samples. The reason is that Na^+ leaching in unsealed samples leads to modification of
512 the microstructure, composition of reaction products and the degree of reaction (compared to
513 sealed cured samples), all of which have a strong influence on the carbonation resistance.
514 These are indirectly supported by the previous study of the authors where it was shown that
515 paste S100 has a different compressive strength development in sealed and unsealed curing
516 conditions [42].

517 It can also be observed that, in unsealed samples, carbonation depth lines do not pass
518 through the origin. While a positive intercept as a result of early carbonation of the paste
519 during curing and preconditioning period can be observed in the paste S0, the other pastes
520 show delayed carbonation. The latest is related to the paste S100 in which the carbonation
521 was only detected after $t=180$ days of exposure. On the other hand, in sealed samples, all the
522 curves pass through the origin besides the paste S100 in which carbonation was not observed.
523 It can also be seen that the propagation rate of carbonation front (slope of the curves)
524 significantly decreased with increasing GBFS content.

525 The carbonation depth seems to be linearly proportional to the square root of time
526 (Fig. 10), that is similar to cement-based materials [43]. This relation is usually described by
527 the Fick's 1st law, whereas the slope of these curves corresponds to the diffusivity constant or
528 carbonation coefficient K ($x=K \cdot t^{0.5}$, where x , carbonation depth; t , time in days).

529 The role of curing conditions in relation to GBFS content on carbonation coefficients
530 is clear in Fig. 11. It seems that there is a certain threshold of GBFS content, after which the
531 curing conditions affect the carbonation rate. This reflects the importance of calcium and

532 shows when the system is rich in GBFS, alkalis play a less important role in carbonation
533 resistance of the samples in the studied carbonation conditions.



534
535 **Fig. 11.** The relationship between carbonation coefficients (K) and GBFS content for the
536 unsealed cured samples and for the sealed cured samples. The carbonation coefficients are
537 calculated using the data in Fig. 10, from linear fits of the carbonation depths as a function of
538 the square root of time ($x=K \cdot t^{0.5}$).

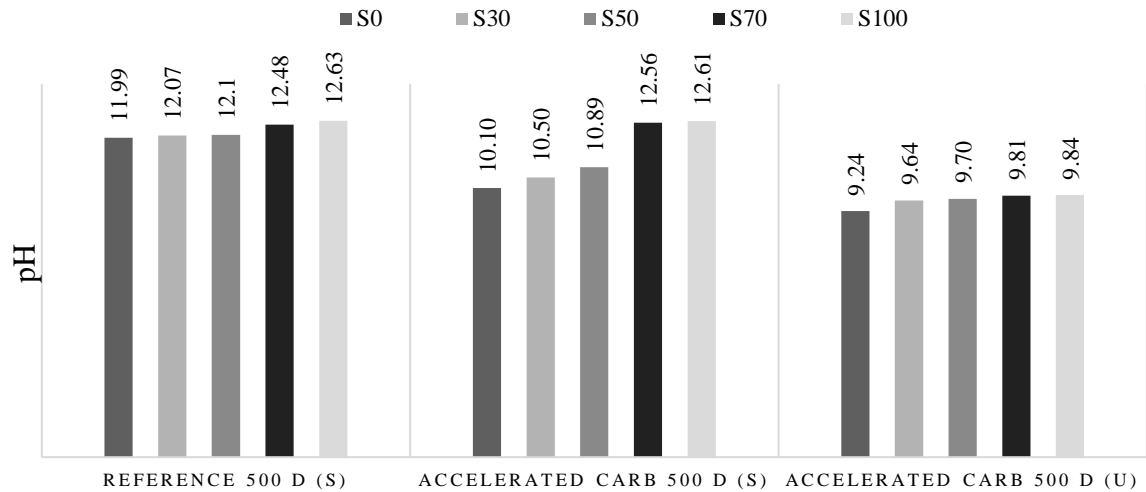
539

540 3.2.2 pH of the pore solution

541

542 The pH of the simulated pore solution of the 500 days sealed cured reference and 500
543 days carbonated samples are presented in Fig. 12.

544

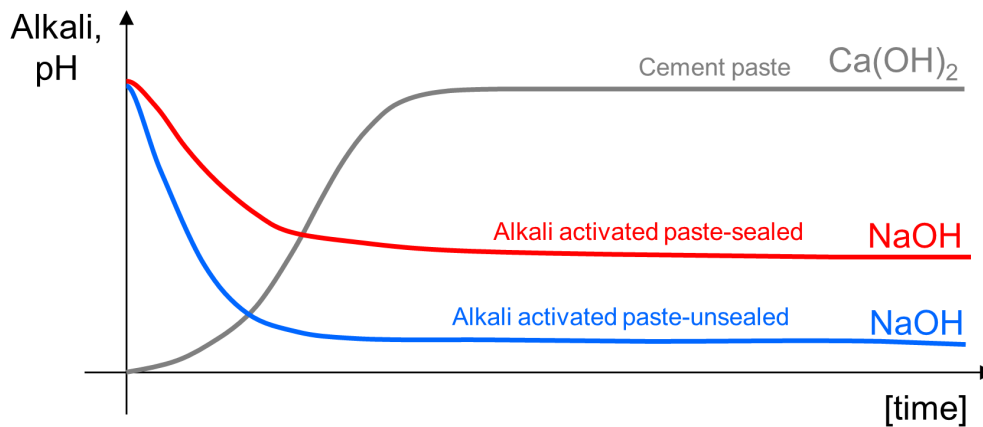


545 **Fig. 12.** pH of simulated pore solutions of alkali-activated pastes as a function of GBFS
 546 content in the paste and curing conditions (500 days cured reference (noncarbonated) pastes
 547 and 500 days under accelerated carbonation, S: sealed samples and U: unsealed samples cured
 548 for 28 days at curing conditions (20 °C, ~99% RH) before their preconditioning and exposure
 549 to accelerated carbonation).
 550

551
 552 At a first glance, it is clear that the pH of the noncarbonated sealed cured pastes
 553 decreased from 13.40 ~ 14.00 at 28 days (see Table 4) to 11.99 ~ 12.63 at 500 days (see Fig.
 554 12). This reduction can be attributed to the consumption of Na^+ and OH^- with the continuous
 555 hydration of the gel, as schematically presented in Fig. 13. A major part of Na^+ and OH^- is
 556 consumed for breaking up the alumino-silicate network of the FA glass (during hydration). In
 557 contrast, breaking up the GBFS network requires lower amount of alkalis. For this reason, the
 558 reduction of pH is higher in FA-rich pastes compared to GFBS-rich pastes. This is in
 559 accordance with a previous study [44] where it was shown that the uptake of Na^+ by the gel
 560 phases increases as the Ca/Si ratio decreases. This also implies that a higher $[\text{Na}^+]$ is expected
 561 to be present in the pore solution of GBFS-rich pastes compared to FA-rich pastes prepared
 562 with the same initial amount of alkaline activator ($\text{S30} < \text{S50} < \text{S70} < \text{S100}$), see Table 4. A
 563 similar change of pH after 1 year of sealed curing was also reported by Pouhet and Cyr [45]

564 for alkali activated metakaoline and by Zuo et al. [46] for alkali activated GBFS. As
 565 schematically shown in Fig. 13, a larger reduction of pH is expected in the unsealed cured
 566 samples due to the leaching of Na^+ from the pore solution. In contrast, the pH buffering agent
 567 in cement-based materials (that is calcium from $\text{Ca}(\text{OH})_2$ and C-S-H) increases until reaching
 568 the maximum degree of hydration and then it remains constant through the time. This ensures
 569 a longer passivation of the reinforcing steel surface when carbonation initiates in cement-
 570 based materials [47] compared to alkali activated pastes.

571



572

573 **Fig. 13.** Schematic illustration of the content of alkali sources in cement paste (grey line,
 574 alkali source: $\text{Ca}(\text{OH})_2$) versus alkali activated paste, sealed (red line, alkali source: NaOH)
 575 and unsealed cured (blue line, alkali source: NaOH) during the hydration process.

576

577 In carbonated sealed cured alkali activated pastes, a clear reduction of pH is observed in
 578 S0, S30 and S50 samples (for example this value is reduced from 11.99 to 10.10 in paste S0).
 579 Meanwhile, the change of pH is negligible in the pastes with high GBFS contents (S70 and
 580 S100). In S100, this was expected because the paste was not carbonated. In paste S70,
 581 however, a reduction of pH was expected. As the carbonation occurred only in the
 582 microcracks of the sample S70, the carbonation front was not uniform and thin. The taken

583 powders were, therefore, a mix of carbonated and noncarbonated parts that led to a high pH.

584 The role of Na^+ consumption is also insignificant in this paste due to the small portion of FA.

585 In unsealed samples, the reduction of pH after carbonation is much more than of the
586 sealed cured samples. The pH of carbonated unsealed pastes, reaches a value of 9.24 in S0
587 and a value of 9.84 in S100. Note that all these pH values are related to the strongly
588 carbonated outer surface material (for pastes S0, S30 and S50). This larger pH reduction is the
589 result of three concurrent mechanisms: continuous FA and GBFS dissolution, Na^+ leaching,
590 and carbonation of NaOH in the pore solution. Carbonation of NaOH is followed by
591 dissolution of the calcium from the C-N-A-S-H gel which acts as a pH buffering agent. In
592 samples with lower GBFS content, the amount of available calcium is less and thus the
593 buffering capacity is less. Therefore, the pH of these samples after carbonation shows a larger
594 reduction. It is assumed that a combination of CaCO_3 and gel phases with remaining Na^+
595 buffers the alkalinity above pH 9 for the GBFS containing pastes. On the other hand, it is
596 likely that the NASH gel and remaining Na^+ buffer the alkalinity for carbonated paste S0.
597 The obtained pH values in all carbonated unsealed cured samples are lower than the predicted
598 pH values of Bernal et al. [19] for the same NaOH content and CO_2 concentration.

599 It is clear that the pH reduction occurs faster in carbonated alkali activated pastes
600 compared to cement-based pastes. The combination of a low $[\text{Na}^+]$ with an eventual Na^+ loss
601 in unsealed curing conditions, leads to a lower pH. This could accelerate corrosion of
602 reinforcing steel in carbonated samples unless the concentration of alkalis in the pore solution
603 remains high at both early and later ages. This latter can be achieved when appropriate curing
604 conditions are followed and the permeability of the material is sufficiently low. The obtained
605 pH values in carbonated unsealed samples (see Fig. 12) are significantly low and near the
606 limit of depassivation of the steel [1]. It should, however, be noted that these results are

607 obtained from alkali activated *pastes*. The effect of carbonation on the pore solution of alkali
608 activated *concrete* needs further study.

609 4. Conclusions

610

611 The effect of curing conditions and GBFS content on the pore solution composition
612 and carbonation resistance of the alkali-activated FA/GBFS pastes was investigated in this
613 study. From the experimental observations, the following conclusions can be drawn:

- 614 • An alkali leaching mechanism was observed in the unsealed cured specimens. This is
615 most likely the result of several counter-affecting mechanisms. The RH difference
616 between the environment and the specimen, causes a capillary flow from the surface to the
617 interior of the samples and, therefore, an inward movement of the ions (advection).
618 Meanwhile, condensation of water on the surface of the samples leads to dilution of the
619 ions at the surface compared to the interior of the specimens. This causes a diffusive
620 movement of ions from the interior towards the surface of the samples. Here, the diffusive
621 outward movement of ions governed the inward advective water movement that in total
622 led to a loss of the alkali from the pore solution.
- 623 • A higher reduction of alkalinity was seen in pastes containing 0, 30, 50 wt.% GBFS in
624 comparison to pastes containing 70 and 100 wt.% GBFS. The main reason is larger
625 consumption of Na^+ and OH^- during FA dissolution in pastes containing a large content of
626 FA. The binding of Na^+ by the gel phases of the alkali activated paste reduces the
627 effective $[\text{Na}^+]$ in the pore solution and hence the alkalinity of the pore solution. The
628 GBFS-rich pastes have a lower Na^+ -binding capacity, hence there is a higher $[\text{Na}^+]$ in the
629 pore solution. This ensures a larger alkalinity buffer of the pore solution once the
630 carbonation occurs in GBFS-rich pastes.

- 631 • Alkali leaching led to a faster propagation rate of carbonation front in unsealed samples.
632 The replacement of FA by GBFS significantly improved the carbonation resistance
633 independent from the curing condition.
- 634 • Based on the results for evolution of pH and propagation rate of carbonation, there are two
635 reasons of pH decrease at long-term:
- 636 – the pH of alkali activated pastes decreased due to ongoing gel formation (from pH
637 13.40 – 14.00 after 28 days of sealed curing to the pH 11.99-12.63 after 500 days
638 (see Fig. 12)).
 - 639 – the pH decreased due to neutralization of the alkalis in the pore solution of the
640 pastes under carbonation.

641 As can be seen, curing may affect the long-term performance of AAMs not only in view
642 of carbonation, but also in view of gel formation at later ages. The availability of alkalis is
643 a first preventive measure for obtaining satisfactory carbonation resistance of AAMs.

- 644 • Since carbonation of AAMs is of a major practical interest, the results presented here
645 show that sealed curing conditions certainly contribute to the production of more durable
646 alkali-activated FA/GBFS materials against carbonation. This is in contrast to the
647 traditional curing of OPC-based concretes, where the curing under water of OPC-based
648 concretes favours the cement hydration, especially in the external layer of the OPC-based
649 concrete specimens.

650 **Acknowledgement**

651 This research was carried out under the project S81.1.13498 in the framework of the
652 Partnership Program of the Materials innovation institute M2i (www.m2i.nl) and the
653 Technology Foundation STW (www.stw.nl), which is part of the Netherlands Organisation
654 for Scientific Research (www.nwo.nl). The first author thanks Rob Polder from Microlab, TU

655 Delft (the Netherlands) for valuable discussions. The second author acknowledges the
656 financial support of the European Union's Marie Curie Individual Fellowship program under
657 REAgrant agreement No. 701531. The authors also thank anonymous reviewers for their
658 comments which substantially improved the quality of this paper.

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660 **References**

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- 662 [1] L. Bertolini, B. Elsener, P. Pedferri, E. Redaelli, R.B. Polder, Carbonation-Induced
663 Corrosion, in: Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair, Second
664 Edition, John Wiley & Sons, 2013, pp. 79-92.
- 665 [2] L.J. Parrott, Damage caused by carbonation of reinforced concrete, Mater. Struct.
666 23(3) (1990) 230-234.
- 667 [3] V.G. Papadakis, C.G. Vayenas, M.N. Fardis, Experimental investigation and
668 mathematical modeling of the concrete carbonation problem, Chem. Eng. Sci. 46(5-6)
669 (1991) 1333-1338.
- 670 [4] A.V. Saetta, B.A. Schrefler, R.V. Vitaliani, The carbonation of concrete and the
671 mechanism of moisture, heat and carbon dioxide flow through porous materials, Cem.
672 Concr. Res. 23(4) (1993) 761-772.
- 673 [5] M. Thiéry, G. Villain, P. Dangla, G. Platret, Investigation of the carbonation front
674 shape on cementitious materials: Effects of the chemical kinetics, Cem. Concr. Res.
675 37(7) (2007) 1047-1058.
- 676 [6] A. Hidalgo, C. Domingo, C. Garcia, S. Petit, C. Andrade, C. Alonso, Microstructural
677 changes induced in Portland cement-based materials due to natural and supercritical
678 carbonation, J. Mater. Sci. 43(9) (2008) 3101-3111.
- 679 [7] K. Arbi, M. Nedeljković, Y. Zuo, G. Ye, A Review on the Durability of Alkali-
680 Activated Fly Ash/Slag Systems: Advances, Issues, and Perspectives. Ind. Eng. Chem.
681 Res. 55(19) (2016) 5439-5453.
- 682 [8] A. Morandau, M. Thiéry, P. Dangla, Investigation of the carbonation mechanism of
683 CH and C-S-H in terms of kinetics, microstructure changes and moisture properties,
684 Cem. Concr. Res. 56(0) (2014) 153-170.
- 685 [9] A. Leemann, P. Nygaard, J.Kaufmann, R. Loser, Relation between carbonation
686 resistance, mix design and exposure of mortar and concrete, Cem. Concr. Compos. 62
687 (2015) 33-43.
- 688 [10] Z. Shi, B. Lothenbach, M.R. Geiker, J. Kaufmann, A. Leemann, S. Ferreira, J.
689 Skibsted, Experimental studies and thermodynamic modeling of the carbonation of
690 Portland cement, metakaolin and limestone mortars, Cem. Concr. Res. 88 (2016) 60-
691 72.
- 692 [11] P.H. Borges, J.O. Costa, N.B. Milestone, C.J. Lynsdale, R.E. Streatfield, Carbonation
693 of CH and C-S-H in composite cement pastes containing high amounts of BFS, Cem.
694 Concr. Res. 40(2) (2010) 284-292.
- 695 [12] Y. Ma, G. Ye, J. Hu, Micro-mechanical properties of alkali-activated fly ash evaluated
696 by nanoindentation, Constr. Build. Mater. 147 (2017) 407-416.

- 697 [13] C.E. White, L.L. Daemen, M. Hartl, K. Page, Intrinsic differences in atomic ordering
698 of calcium (alumino) silicate hydrates in conventional and alkali-activated cements,
699 *Cem. Concr. Res.* 67 (2015) 66-73.
- 700 [14] R.J. Myers, S.A. Bernal, R. San Nicolas, J.L. Provis, Generalized structural
701 description of calcium–sodium aluminosilicate hydrate gels: the cross-linked
702 substituted tobermorite model, *Langmuir*, 29(17) (2013) 5294-5306.
- 703 [15] M.B. Haha, B. Lothenbach, G. Le Saout, F. Winnefeld, Influence of slag chemistry on
704 the hydration of alkali-activated blast-furnace slag - Part I: Effect of MgO, *Cem.*
705 *Concr. Res.* 41(9) (2011) 955-963.
- 706 [16] M. Palacios, F. Puertas, Effect of Carbonation on Alkali-Activated Slag Paste, *J. Am.*
707 *Ceram. Soc.* 89(10) (2006) 3211-3221.
- 708 [17] F. Puertas, M. Palacios, T. Vázquez, Carbonation process of alkali-activated slag
709 mortars, *J. Mater. Sci.* 41(10) (2006) 3071-3082.
- 710 [18] S.A. Bernal, R.M. de Gutiérrez, A.L. Pedraza, J.L. Provis, E.D. Rodriguez, S.
711 Delvasto, Effect of binder content on the performance of alkali-activated slag
712 concretes, *Cem. Concr. Res.* 41(1) (2011) 1-8.
- 713 [19] S.A. Bernal, J.L. Provis, D.G. Brice, A. Kilcullen, P. Duxson, J.S. van Deventer,
714 Accelerated carbonation testing of alkali-activated binders significantly
715 underestimates service life: The role of pore solution chemistry, *Cem. Concr. Res.*
716 42(10) (2012) 1317-1326.
- 717 [20] S.A. Bernal, J.L. Provis, B. Walkley, R. San Nicolas, J.D. Gehman, D.G. Brice, A.R.
718 Kilcullen, P. Duxson, J.S. van Deventer, Gel nanostructure in alkali-activated binders
719 based on slag and fly ash, and effects of accelerated carbonation, *Cem. Concr. Res.* 53
720 (0) (2013) 127-144.
- 721 [21] S.A. Bernal, R. San Nicolas, R.J. Myers, R.M. de Gutiérrez, F. Puertas, J.S. van
722 Deventer, J.L. Provis, MgO content of slag controls phase evolution and structural
723 changes induced by accelerated carbonation in alkali-activated binders, *Cem. Concr.*
724 *Res.* 5(0) (2014) 33-43.
- 725 [22] M. Nedeljković, B. Šavija, Y. Zuo, M. Luković, G. Ye, Effect of natural carbonation
726 on the pore structure and elastic modulus of the alkali-activated fly ash and slag
727 pastes. *Constr. Build. Mater.*, 161 (2018) 687-704.
- 728 [23] N. Li, N. Farzadnia, C. Shi, Microstructural changes in alkali-activated slag mortars
729 induced by accelerated carbonation, *Cem. Concr. Res.* 100 (2017) 214-226.
- 730 [24] S.A. Bernal, J.L. Provis, R.M. De Gutiérrez, J.S. van Deventer, Accelerated
731 carbonation testing of alkali-activated slag/metakaolin blended concretes: effect of
732 exposure conditions, *Mater. Struct.* (2014) 1-17.
- 733 [25] F.R. Škvára, V. Šmilauer, P.E. Hlaváček, L.U. Kopecký, Z. Cilova. A weak alkali
734 bond in (N, K)–A–S–H gels: evidence from leaching and modeling, *Ceram Silik*,
735 56(4) (2012) 374-382.
- 736 [26] R.R. Lloyd, J.L. Provis, J.S.J. van Deventer, Pore solution composition and alkali
737 diffusion in inorganic polymer cement, *Cem. Concr. Res.* 40(9) (2010) 1386-1392.
- 738 [27] N. Ukrainczyk, O. Vogt, E.A. Koenders, Reactive Transport Numerical Model for
739 Durability of Geopolymer Materials, *Advances in Chemical Engineering and Science*,
740 6(04) (2016) 355.
- 741 [28] H. Huang, G. Ye, Examining the “time-zero” of autogenous shrinkage in high/ultra-
742 high performance cement pastes, *Cem. Concr. Res.* 97 (2017) 107-114.

- 743 [29] J. Kempl, O. Çopuroğlu, EH-pH- and main element analyses of Blast Furnace Slag
744 Cement paste pore solutions activated with sodium monofluorophosphate –
745 Implications for carbonation and self-healing, *Cem. Concr. Compos.* 71 (2016) 63-76.
- 746 [30] M. Babae, M.S.H. Khan, A. Castel, Passivity of embedded reinforcement in
747 carbonated low-calcium fly ash-based geopolymer concrete. *Cem. Concr. Compos.*
748 85(Supplement C) (2018) 32-43.
- 749 [31] Y. Ma, J. Hu, G. Ye, The pore structure and permeability of alkali activated fly ash.
750 *Fuel* 104 (2013) 771-780.
- 751 [32] M. Nedeljković, K. Arbi, Y. Zuo, G. Ye, Microstructural and mineralogical analysis of
752 alkali activated fly ash-slag pastes. The 3rd International RILEM Conference on
753 Microstructure Related Durability of Cementitious Materials (2016) Nanjing, China,
- 754 [33] C. Dow, F.P. Glasser, Calcium carbonate efflorescence on Portland cement and
755 building materials. *Cem. Concr. Res.* 33(1) (2003) 147-154.
- 756 [34] Z. Li, M. Nedeljković, Y. Zuo, G. Ye, Autogenous shrinkage of alkali-activated slag –
757 fly ash pastes, in 5th International Slag Valorisation Symposium (2017) Leuven,
758 Belgium.
- 759 [35] Z. Jiang, Z. Sun, P. Wang, Internal relative humidity distribution in high-performance
760 cement paste due to moisture diffusion and self-desiccation. *Cem. Concr. Res.* 36(2)
761 (2006) 320-325.
- 762 [36] M. Nedeljković, K. Arbi, Y. Zuo, G. Ye, Physical properties and pore solution
763 analysis of alkali-activated fly ash-slag pastes, International RILEM Conference
764 Materials Systems and Structures in Civil Engineering (2016) Lyngby, Denmark.
- 765 [37] M. Nedeljković, K. Arbi, Y. Zuo, G. Ye, CO₂ binding capacity of alkali-activated fly
766 ash and slag pastes. *Ceram. Int.* (2018)
- 767 [38] Z. Zhang, J.L. Provis, A. Reid, H. Wang, Fly ash-based geopolymers: The relationship
768 between composition, pore structure and efflorescence, *Cem. Concr. Res.*
769 64(Supplement C) (2014) 30-41.
- 770 [39] J. García Carmona, J. Gómez Morales, R. Rodríguez Clemente, Rhombohedral–
771 scalenohedral calcite transition produced by adjusting the solution electrical
772 conductivity in the system Ca(OH)₂–CO₂–H₂O. *J. Colloid Interface Sci.* 261(2)
773 (2003) 434-440.
- 774 [40] H.F. Taylor, *Cement chemistry*, second ed. Thomas Telford, 1997.
- 775 [41] J B. Jones, X. Peng, Hot spring deposits on a cliff face: A case study from Jifei,
776 Yunnan Province, China, *Sediment. Geol.* 302 (2014) 1-28.
- 777 [42] M. Nedeljković, Y. Zuo, K. Arbi, G. Ye, Carbonation Resistance of Alkali-Activated
778 Slag Under Natural and Accelerated Conditions. *Journal of Sustainable Metallurgy*,
779 4(1) (2018) 33-49.
- 780 [43] I.S. Yoon, O. Çopuroğlu, K.B. Park, Effect of global climatic change on carbonation
781 progress of concrete, *Atmos. Environ.* 41(34) (2007) 7274-7285.
- 782 [44] R.J. Myers, J.L. Provis, B. Lothenbach, Composition–solubility–structure
783 relationships in calcium (alkali) aluminosilicate hydrate (C-(N, K-)ASH), *Dalton*
784 *Trans.* 44(30) (2015) 13530-13544.
- 785 [45] R. Pouhet, M. Cyr, Carbonation in the pore solution of metakaolin-based geopolymer.
786 *Cem. Concr. Res.* 88 (2016) 227-235.
- 787 [46] Y. Zuo, M. Nedeljković, G. Ye, Coupled thermodynamic modelling and experimental
788 study of sodium hydroxide activated slag. *Constr. Build. Mater.* 188 (2018) 262-279.

789 [47] J.H.M. Visser, Influence of the carbon dioxide concentration on the resistance to
790 carbonation of concrete. *Constr. Build. Mater.* 67 (2014) 8-13.

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