

1 **Mortars with alkali-activated municipal solid waste incinerator bottom ash**
2 **and fine recycled aggregates**

3 S. Casanova¹, R. V. Silva^{2*}, J. de Brito³, M. F. C. Pereira⁴

4 1 Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
5 (e-mail: sofia3casanova@gmail.com)

6 2 CERIS, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
7 (*Corresponding author e-mail: rui.v.silva@tecnico.ulisboa.pt)

8 3 CERIS, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
9 (e-mail: jb@civil.ist.utl.pt)

10 4 CERENA, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
11 (e-mail: mfc@ist.utl.pt)

12
13 **Abstract:** Milled municipal solid waste incinerator bottom ash was used as a precursor in the
14 production of alkali-activated mortars with recycled concrete aggregates as a sand substitute.
15 Fly ash was used as control precursor and sodium hydroxide as an alkaline activator. Different
16 thermal curing regimens were used: 24 h in ambient conditions; 24 h/70 °C; 48 h/70 °C; and
17 24 h/90 °C. Mechanical and durability-related performances were evaluated (i.e. flexural and
18 compressive strength, modulus of elasticity, ultrasonic pulse velocity, carbonation, capillary
19 water absorption, and shrinkage). The reaction between metallic aluminium from municipal
20 solid waste incinerator bottom ash and OH⁻ ions produced hydrogen gas, causing expansion,
21 porosity increase and thus decline in performance. Low stability in high relative humidity set-
22 tings due to leaching of highly soluble compounds was also observed. A further decline in
23 performance was observed in mixes containing recycled aggregates. Alkali activated municipal
24 solid waste incinerator bottom ash presented fast carbonation but also a considerable strength
25 enhancement.

26 **Keywords:** municipal solid waste; incinerator bottom ash; alkali-activated materials; recycled
27 aggregates; curing conditions.

28 **Declarations of interest:** none

29 **1 Introduction**

30 Alkali-activated materials (AAM), which have been regarded as one of the best alternatives to ce-
31 ment in concrete and mortar production, are the product of a reaction between a solid aluminosili-
32 cate (i.e. precursor) in an alkaline medium (i.e. alkali activator) (Provis, 2018). The solid precursor
33 usually consists of aluminosilicate supplementary cementitious materials, including ground granu-
34 lated blast furnace slag (GGBS), coal fly ash (FA), calcined clays and natural pozzolans, having
35 demonstrated good results (Provis and van Deventer, 2014). Geopolymers, which share the concept
36 of production with AAM (i.e. dissolution of the precursors' amorphous phases using a strongly
37 alkaline solution), though exhibiting polymeric systems and mechanical behaviour, have shown a
38 considerable ability to immobilize heavy metals, fast setting at room temperature, high resistance
39 to acid attack and high compressive strength (Davidovits, 1994). Furthermore, despite some varia-
40 bility in the values in the literature, life cycle assessments demonstrated 55-75% lower CO₂ emis-
41 sions when compared to equivalent cement-based materials (Yang et al., 2013).

42 Since there has been a shift towards renewable sources, the generation of FA has been declin-
43 ing, which will naturally affect potential supply chains for AAM based on FA (Rowlatt, 2019).
44 Additionally, though the production of new steel relies on blast furnaces, metal recycling in
45 electric arc furnaces is preferred due to their higher efficiency, thereby decreasing GGBS pro-
46 duction (Singh, 2012; Zhong, 2018). For this reason, there is considerable scope in studying
47 other solid precursors for AAM production.

48 In Europe, about 20 million tonnes of MSW are produced each year (Nørgaard et al., 2019). The
49 incineration of this waste results in two by-products - fly ash and bottom ash. The former is
50 generally comprised of hazardous compounds and must be treated before their application or safe
51 disposal (Ferraro et al., 2019). The incinerator bottom ash from MSW (MIBA) represents 85-
52 95% of the incineration products (Dhir et al., 2018). It is a highly siliceous by-product, with a

53 notable amount of calcium-based phases as well as alumina and iron oxides (Kurda et al., 2020),
54 capable of being valorised in the production of AAM, which can therefore reduce its landfilling
55 (Silva et al., 2017). The existing studies on the alkali activation of MIBA show that it is reactive
56 to the presence of a strongly alkaline medium, though not without its limitations. In the study of
57 Chen et al. (2016), wherein alkali-activated MIBA was used to produce aerated specimens, alka-
58 line solutions with different concentrations of NaOH were used (2 M, 4 M, 8M and 12 M). The
59 authors adopted different mix durations, ranging from 15 to 120 min, to potentiate the corrosion
60 of metallic Al, which is present in a relatively great amount in MIBA. This corrosion is known
61 to result in the production of H₂ gas, which is meant to be the aerating agent in this case. An
62 alkaline solution with a concentration of 8 M and mixing time of 60 min revealed to optimal to
63 enhance the mechanical performance and porosity.

64 In the study of Galiano et al. (2011), FA and MIBA were used as solid precursors (74% and
65 26%, by weight, respectively, of the total binder). Different contents of NaOH, KOH (~4% by
66 weight of the precursors), Na₂SiO₃ and K₂SiO₃ (~21% by weight of the precursors) were used
67 as activators. The specimens were cured in ambient conditions and at a temperature of 60 °C.
68 Relatively low compressive strength was observed in all specimens regardless of the activator,
69 with a maximum of 7 MPa and almost all below 1 MPa. Although it was not stated by the
70 authors, this low performance was probably due to the formation of H₂ gas from the reaction
71 of Al with the OH⁻-rich solution. Specimens cured at 60 °C exhibited higher strength than that
72 of those cured at ambient temperature.

73 Cristelo et al. (2020) produced pastes using varying concentrations of NaOH (4-12 molal) in the
74 alkaline activator as well as with the incorporation of sodium silicate (SiO₂/Na₂O weight ratio of
75 2.0) for the activation of MIBA and/or fly ash from MSW incineration. Liquid to solid ratios
76 varied between 0.35 and 0.50. Compressive strength values of mixes with NaOH alone were low
77 (between 1.5 MPa and 3 MPa) but increased with the use of sodium silicate (over 10 MPa). The

78 decline in performance was mostly due to the extensive expansion caused by the reaction of Al
79 with the NaOH solution. When exposed to wetting and drying cycles, specimens with a 4 m
80 NaOH activator exhibited quite low stability, demonstrating severe mass loss after each cycle.

81 Huang et al. (2018) assessed the influence of different curing methods on the performance of mor-
82 tars containing alkali-activated 60 wt% MIBA and 40 wt% GGBS. The alkali activator was a com-
83 bination of 4.8 M NaOH solution and Na_2SiO_3 with a modulus of 2.6 (weight proportions of the
84 total solution of 55% and 44%, respectively). The methods consisted of natural curing (5-20 °C
85 and 60% RH), standard curing room (20 ± 2 °C and > 95% RH), seal curing (20 ± 2 °C and > 95%
86 RH), steam curing (80 ± 2 °C and > 100% RH) and soaking curing (20 ± 2 °C and 100% RH). 28-
87 day compressive strength varied between 28 MPa and 53 MPa, depending on the curing method.
88 The authors observed that natural and soaking curing methods yielded lower strength due to leach-
89 ing of OH^- , which led to a reduction of pH and thus lower dissolution of active components. The
90 optimum performance was observed in samples cured in high RH environment, yet with low con-
91 tact with external water (i.e. seal and standard curing methods).

92 Huang et al. (2020) studied the effect of increasing NaOH content (1.7%, 5.6% and 11.1% by
93 weight of total precursor) of mortars containing alkali-activated MIBA and GGBS. The sodium
94 silicate solution (9.65% Na_2O , 25.22% SiO_2 , and 65.13% H_2O) content was constant and about
95 27% of the binder's weight, to which water and NaOH were added. Increasing the amount of
96 NaOH content led to higher pH levels, which translated into a more effective dissolution of
97 aluminosilicate phases and thus improved strength development (47.4 MPa for mixes with
98 NaOH content of 5.55% that of the weight of the precursors). 28-day compressive strength of
99 27.9 MPa and 36.5 MPa were observed for mixes containing about 2% and 11% of NaOH,
100 respectively, indicating optimum levels in between. Through a conversion rule between free
101 and “union” alkali, the authors demonstrated that, for a given amount of total alkali incorpo-
102 rated in the mortars, there was a considerable loss of alkali in mixes made with sodium silicate

103 alone to the external environment (diffusion mechanism to achieve equilibrium with an efflo-
104 rescence phenomenon). The amount of “union” alkali, which corresponds to that of resulting
105 from the polymerization process, was higher for mixes with a 5.55% NaOH content.

106 Atiş et al. (2015) analysed the influence of the curing conditions of AAM based on class F FA. All
107 mixes were designed with an aggregate/FA ratio of 3 and water/FA ratio of 1/3. The authors stated
108 that alkali activators with various concentrations of Na⁺ (4% to 20% by weight of the precursor
109 with 2% increment) from a 97% pure NaOH. The specimens tested had different combinations of
110 curing temperatures (varying between 45 °C and 115 °C), ratios of Na⁺/FA (4-20%) and curing
111 time (24 h, 48 h, 72 h). Increasing the curing period from 24 h to 48 h led to a generalised strength
112 increase, though equivalent results were observed by increasing up to 72 h. The optimum perfor-
113 mance was observed in specimens cured in 115 °C for 24 h, and with a Na⁺/FA ratio of 14% (com-
114 pressive and flexural strengths of 120 MPa and 15 MPa were, respectively, observed). No strength
115 gain was observed for curing temperatures of 45 °C. On the other hand, in several cases of speci-
116 mens cured at 115 °C, no strength gain was observed. This was attributed to fast evaporation of the
117 solvent, which may have prevented the adequate dissolution of the FA’s particles.

118 Fang et al. (2018) analysed the performance of FA/GGBS-based alkali-activated concrete
119 cured at ambient temperature. GGBS content varied between 10% and 30% by weight of the
120 total binder. The alkaline solution to binder ratio was set at 0.4 and the molarity of NaOH
121 varied between 10 M and 12 M. The ratio between the Na₂SiO₃ and NaOH was kept constant
122 at 2. All mixes presented setting at ambient conditions (initial and final setting times were
123 found to be in the range of 80-350 min and 100-470 min, respectively). The incorporation of
124 GGBS significantly reduced setting time. Specimens with 30% GGBS presented a higher
125 strength gain over time, reaching 56 MPa after 28 days, whereas those with 10% GGBS and
126 90% FA showed a compressive strength of about 22 MPa, in the same period.

127 Regarding the effect of incorporating recycled aggregates (RA) in AAM, little research has
128 been carried out. In the study of Alonso et al. (2018), mortars were produced using RA from
129 crushed concrete and ceramic particles. The precursors for AAM were GGBS and FA, and
130 conventional mortars using cement were also produced. The activator for the GGBS mixes was
131 a sodium silicate and sodium hydroxide solution ($\text{Na}_2\text{O} \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O} + \text{NaOH}$) with a
132 $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 1.2 and 4% Na_2O by mass of the precursor. For FA mixes, the activator was
133 a 10 M NaOH solution plus 15% sodium silicate solution. GGBS- and FA-based mortars pre-
134 sented 28-day compressive strength values of about 91 MPa and 24 MPa, respectively, whereas
135 the control cement mortar showed a compressive strength of about 75 MPa. As expected, the
136 incorporation of RA led to a decline of mechanical performance. Regardless of the binder,
137 losses of 40-50% and 60-70% in the 28-day compressive strength were observed for mixes
138 with 100% RA from crushed concrete and ceramic bricks, respectively.

139 Nuaklong et al. (2016) evaluated the influence of coarse RA from crushed concrete in mixes with
140 alkali-activated FA. The activator was comprised of a fixed content of 162 kg/m^3 of aqueous
141 Na_2SiO_3 and 108 kg/m^3 of a NaOH solution with different concentrations (i.e. 8 M, 12 M and 16
142 M). Specimens were subjected to 60°C curing temperature for 2 days and subsequently placed
143 in a controlled environment at 23°C and 50% RA for 7 days. The compressive strength of control
144 specimens was marginally affected with varying concentration of the NaOH solution. However,
145 this parameter was more sensitive to the incorporation of RA; mixes with 8M, 12 M and 16 M
146 NaOH solutions showed compressive strength values of 30.6 MPa, 38.4 MPa and 34.8 MPa,
147 respectively (76%, 93% and 87%, respectively, when compared with the FA mixes).

148 This study is part of a state-funded research project in Portugal, connecting corporations within
149 the construction sector, intending to further reduce the environmental impact and cost associ-
150 ated with the production of structural concrete by means of the alkali activation of MIBA as

151 integral replacement of cement and RA as a substitute of sand. The purpose of this study was
152 to evaluate the performance of alkali-activated mortars subjected to different curing conditions,
153 with MIBA as the precursor to obtain a stable product with enough mechanical performance.
154 The literature review shows that few studies were carried out on the influence of different cur-
155 ing regimens of MIBA-based AAM with none on MIBA as the sole precursor and that only
156 one relevant study was made on AAM containing RA from construction and demolition waste.
157 The behaviour of some of the mortars in this study is compared with that of cement mortars
158 and alkali-activated mortars with FA as the precursor. X-ray fluorescence (XRF) and powder
159 XRD analyses were carried out on cement, FA, MIBA and selected mortars. The specimens'
160 mechanical and durability-related performances were evaluated through their flexural and com-
161 pressive strength, ultrasonic pulse velocity, modulus of elasticity, carbonation, water absorp-
162 tion by capillary action, and shrinkage.

163 **2 Materials and test methods**

164 **2.1 Cement and precursors**

165 Cement CEM I 42.5R was used as the control for conventional mortars. The alkaline activator
166 (AA) was a solution of water and NaOH (99% purity), with mass percentages of 71.4% and
167 28.6%, respectively (10 m NaOH solution). Class F coal FA (ASTM-C618, 2019), provided
168 by the Portuguese cement producer Secil, was used as the control binder for AAM. MIBA was
169 sourced from the Valorsul's MSW treatment plant, located in São João da Talha, in the munic-
170 ipality of Loures, Portugal. This waste-to-energy power plant is a moving grate furnace that
171 treats undifferentiated waste from households in the Great Metropolitan Area of Lisbon. In
172 mortars with MIBA, lignosulphonate-based water-reducing admixture was used (2% of Si-
173 kament 400 Plus by weight of binder). X-ray fluorescence (XRF) analysis was carried out on
174 cement, MIBA and FA. For the first two, XRF analysis was made with a Niton XL3T GOLDD

175 spectrometer from Thermo Scientific with an X-ray generator of 50 kV/200 μ A, equipped with
176 a CCD for image location (3 mm spot diameter) and storage, whereas the latter's composition
177 was obtained by wavelength dispersive XRF, using an S4 Pioneer apparatus of BRUKER, with
178 a potential of 4 kV. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and quantification of magnetic metal and metallic aluminium fractions were carried out for additional characterization of MIBA. The fraction of metallic aluminium was quantified through the stoichiometry of the reaction of MIBA in a 2.5 M NaOH solution. The amount of H₂ gas released from this reaction was measured and compared with a control test comprising metallic Al alone. The pozzolanicity of MIBA and FA was quantified using the Chapelle test (Ferraz et al., 2015; NBR-15895, 2010). The water used in the production of all specimens was potable tap water complying with Directive 98/83/CE (CEU, 1998).

186 **2.2 Aggregate and mortar test methods**

187 The natural aggregates (NA) were siliceous fine and coarse sands (0/1 and 0/4, respectively),
188 whereas the RA was sourced from crushed concrete produced at the Construction Laboratory
189 at IST. At least three samples of each material/mortar mix were analysed for every test presented in this paper. The aggregates' particle size distribution test was carried out as per EN 1015-1 (EN-1015-1, 1999). The bulk density was tested according to EN 1097-3 (EN-1097-3, 1998), and water absorption and apparent densities with EN 1097-6 (EN-1097-5, 2008). The dynamic behaviour of water absorption by RA was evaluated by means of the test method presented in Rodrigues et al. (Rodrigues et al., 2013), to calculate the amount of compensating water. This method consists of measuring the water absorbed by fine RA over time in a hydrostatic scale using a sodium hexametaphosphate [(NaPO₃)₆] solution. This dispersant was used in this test method to prevent agglomeration of particles, which is a phenomenon that typically occurs during this test and that hinders the measurement of water absorption.

199 The production of mortar specimens was based on EN 1015-2 (EN-1015-2, 1999). The consist-
200 ence of fresh mortars was evaluated as per EN 1015-3 (EN-1015-3, 1999). The performance of
201 mortars in the hardened state was evaluated according to bulk density (EN 1015-6 (EN-1015-6,
202 1999)), dynamic Young's modulus (ASTM E1876 (ASTM-E1876, 2015)), ultrasonic pulse ve-
203 locity (EN 12504-4 (EN-12504-4, 2004)), flexural and compressive strength (EN 1015-11 (EN-
204 1015-11, 1999)), carbonation (LNEC E391 (LNEC-E391, 1993)), water absorption by capillary
205 action (EN 1015-18 (EN-1015-18, 2002)), and shrinkage (EN 1015-13 (EN-1015-13, 1993)).

206 The mortars' constituents and the resulting specimens (dried and ground just after being tested)
207 were analysed by means of XRD patterns using a Bruker D8 Discover A25 instrument with
208 Cu-K α radiation. Diffraction patterns were obtained by scanning the goniometer from 10° to
209 80° (2 θ) at a rate of 0.05°·s⁻¹.

210 **2.3 Mix design**

211 The production of all mortars (total of 336 specimens with a standard size of 40 mm × 40 mm ×
212 160 mm; 21 specimens per type of mix) followed the guidelines of EN 196-1 (EN-196-1, 2005),
213 but for alkali-activated MIBA mortars, extended mixing time was required to potentiate corro-
214 sion of metallic aluminium (15 min mixing + 45 min resting before placing in the moulds vs. 4
215 min as expressed in EN-196-1 (2005)). Minimal loss of workability and no setting were observed
216 during this extended mixing time thereby suggesting marginal precipitation of reaction products.
217 A slight adaptation was also required for mixes with RA to allow the absorption of compensating
218 water; RA were mixed with 2/3 of the total effective water for 5 min before adding the rest of the
219 components. The method adopted for the mix design yields mortars exhibiting characteristics
220 and performance equivalent to those of a concrete counterpart and not mortars typically used for
221 rendering and masonry. All mortars have a volumetric proportion of binder/aggregates of 1/3. A
222 liquid/binder ratio of 0.5 was used to compare mortars made with cement, FA and MIBA. A ratio

223 of 0.65 was applied to analyse MIBA mortars alone, with a variation of the RA fraction. Further
 224 explanation of this variation is in section 3.2.1.

225 Concerning the curing conditions, all specimens were cured for 24 h in the laboratory (sealed
 226 curing with plastic film around the moulds). After that, samples were cured in different envi-
 227 ronments: 24 hours in ambient conditions (~18 °C and RH of ~65%); 24 hours at 70 °C; 48
 228 hours at 70 °C; and 24 hours at 90 °C. After the thermal curing, all specimens were stored in
 229 an environmental chamber with a constant temperature of 20 °C and RH of 60% until testing
 230 age (the total age of the specimens corresponds to the time from the moment of production
 231 until testing). Table 1 provides the mix code for the alkali-activated mortars; FA-NA and FA-
 232 RA correspond to alkali-activated FA mortars, whereas BA-NA and BA-RA are alkali-acti-
 233 vated MIBA mortars. It should be noted that none of the MIBA-based mortars cured in ambient
 234 conditions exhibited setting after one week and thus could not be further characterized.

235 Table 1 - Mix code for alkali-activated mortars

Mix code	Binder	Aggregate	Curing
FA-NA 70/24	Fly ash	Natural aggregates	70 °C for 24 h
FA-NA 70/48			70 °C for 48 h
FA-NA 90/24			90 °C for 24 h
FA-RA 70/24		Recycled aggregates	70 °C for 24 h
FA-RA 70/48			70 °C for 48 h
FA-RA 90/24			90 °C for 24 h
BA-NA 70/24	Bottom ashes from MSW incineration	Natural aggregates	70 °C for 24 h
BA-NA 70/48			70 °C for 48 h
BA-NA 90/24			90 °C for 24 h
BA-RA 70/24		Recycled aggregates	70 °C for 24 h
BA-RA 70/48			70 °C for 48 h
BA-RA 90/24			90 °C for 24 h

236

237 3 Results and discussion

238 3.1 Material characterization

239 3.1.1 Cement and precursors

240 Table 2 presents the composition of the main oxides of the binders from the XRF analysis. The
 241 composition of FA is what one would expect from a Class F; the sum of $Al_2O_3 + SiO_2 + Fe_2O_3$

242 is equal to 84.8% and exceeds the minimum value established (i.e. 70% by weight) following
 243 EN 450-1 (EN-450-1, 2012). The composition of MIBA shows lower content of Al₂O₃ and
 244 Fe₂O₃ and a considerably larger fraction of CaO. According to ASTM C618, MIBA could be
 245 classified as class C FA, wherein the minimum value of the sum of Al₂O₃, SiO₂ and Fe₂O₃ is
 246 50 wt%. It has been shown that about 66% of the MIBAs in the literature satisfy this limit
 247 (Lynn et al., 2017). An additional characterization based on the magnetic separation (using a
 248 neodymium magnet) of a random sample of MIBA (24 g), showed that about 12% and 88%
 249 were magnetic and non-magnetic residues, respectively. This shows that the electromagnetic
 250 separation stage applied at the MIBA's treatment facility was not optimized and further quan-
 251 tities of material could be recovered. Even though the quantification of amorphous Fe phases
 252 was not carried out, a notable amount may be present considering the overall quantity of total
 253 Fe-bearing phases. Future analysis will be carried out on this aspect since amorphous Fe phases
 254 inhibit the dissolution of Si and Al phases (Chen-Tan et al., 2009), thus hindering the strength
 255 development of the resulting mortars.

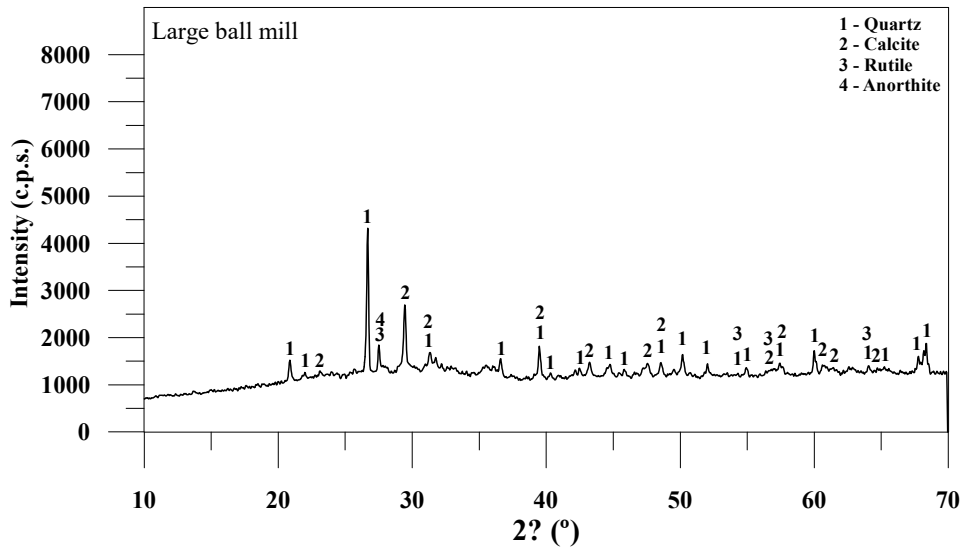
256 Table 2 - XRF of cement, FA and MIBA

Material	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	CaO (%)	MgO (%)	SO ₃ (%)	K ₂ O (%)	TiO ₂ (%)	CuO (%)	Na ₂ O (%)	P ₂ O ₅ (%)
Cement	19.49	5.02	3.32	63.48	1.26	3.26	-	-	-	-	-
FA	51.93	18.75	15.96	4.46	0.90	-	3.24	2.39	1.60	0.76	-
Original	51.84	5.00	9.29	23.00	2.36	2.42	1.57	0.34	0.16	-	2.29
MIBA Magnetic	14.92	4.71	62.61	9.86	2.57	1.36	0.48	0.58	0.15	-	1.26
Non-magnetic	53.74	4.49	6.69	24.25	2.33	2.42	1.60	0.33	0.18	-	2.23

257

258 After ball mill processing (GEOLAB-IST), MIBA exhibited an average particle size under 45 µm.
 259 The XRD analysis (Figure 1) of the milled MIBA showed that it contains some amorphous fraction
 260 (broad reflexion peak between the 15° and 40° 2θ positions), which can be mostly attributed to the
 261 waste glass fraction. This was confirmed by stereomicroscopic observations of the unprocessed
 262 MIBA (Figure 2). The XRD spectrum primarily show quartz peaks (SiO₂ - International Centre for
 263 Diffraction Data - ICDD # 33-1161). Other mineralogical phases included calcite (CaCO₃ - ICDD

264 # 05-0586), rutile (ICDD # 21-1276) and anorthite ([Ca, Na][Si, Al]₄O₈ - ICDD # 20-0020). XRD
265 analysis was also carried out on the two phases resulting from the magnetic separation stage. The
266 non-magnetic fraction showed main peaks of quartz, calcite and anorthite, whereas the magnetic
267 fraction showed peaks of magnetite (Fe₃O₄ - ICDD # 03-0863) and kamacite (Fe, Ni - ICDD # 37-
268 0474).



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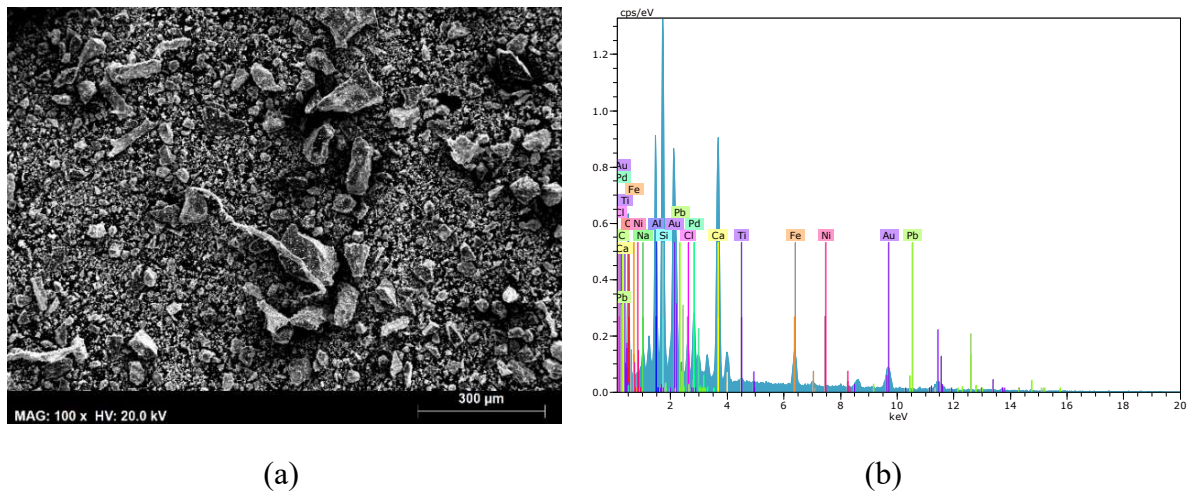
Figure 1 - XRD of MIBA processed in a large ball mill machine



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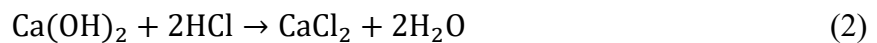
Figure 2 - Stereomicroscopic image of a sample of washed MIBA

275 The morphology of MIBA can be seen in Figure 3a. The particles are irregular and have an
 276 angular shape, which can affect the workability of mixes. The semi-quantitative EDS results
 277 (Figure 3b), based on an elemental mapping of the central area of the specimen, show that the
 278 mass elemental composition of MIBA is mostly comprised of oxygen (~23%), followed by
 279 calcium (~15%), silicon (~9%), aluminium (~7%) and iron (~4%).



280 Figure 3 - SEM (a) and EDS (b) of ground MIBA

281 The pozzolanicity of MIBA and FA was further characterized by the use of the modified
 282 Chapelle test. It determined the content of unconsumed $\text{Ca}(\text{OH})_2$, by titration with 0.1 M HCl
 283 (reactions in equation 1 and 2), by the reactive phases present in FA and MIBA during 16 h of
 284 reaction at $90 \pm 5 \text{ }^\circ\text{C}$ of 2 g CaO grade laboratory and one gram of the precursor diluted in
 285 distilled water.

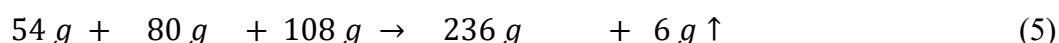
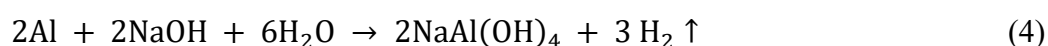


286 The following calculates the amount of mg $\text{Ca}(\text{OH})_2$ / g of precursor (NBR-15895, 2010).

$$\frac{\text{mg Ca}(\text{OH})_2}{\text{g precursor}} = \frac{28 \cdot (v_3 - v_2) \cdot F_c}{m_2} \times 1.32 \quad (3)$$

287 Where m_2 is the mass of the pozzolanic material (g), v_2 the volume of HCl consumed by the
 288 sample (ml); v_3 the volume of HCl consumed by the blank without MIBA as reference (ml); F_c
 289 the correction factor for a 0.1 M solution (ratio between the theoretical and experimental volumes
 290 of consumed HCl); and 1.32 the relation between the molecular masses of $\text{Ca(OH)}_2 / \text{CaO}$. The
 291 results showed values of 566 ± 59 mg and 445 ± 99 mg of $\text{Ca(OH)}_2 / \text{g}$ of FA and MIBA, respec-
 292 tively. Although the average values are higher than the minimum limit of 436 mg $\text{Ca(OH)}_2 / \text{g}$ of
 293 addition, established by Raverdy et al. (1980) for the classification of pozzolanic mineral addi-
 294 tions, the standard deviation corresponding to MIBA suggests that some may be below the thresh-
 295 old. Future evaluation in this regard is warranted considering a much larger sample size (e.g.
 296 MIBA with changing age, various sizes and from different batches).

297 The amount of metallic Al was measured by means of its reaction with aqueous NaOH in an in-
 298 verted test tube, which was connected through a glass tubing to a three-nozzle balloon. Equation
 299 4 shows the chemical reaction behind this process and, in terms of the stoichiometric quantities
 300 (atomic and molecular weights), the quantities of each of the reactants and products generated
 301 in grams are presented in equation 5:



302 Through the stoichiometry of the reaction, the measured volume of released H_2 allowed calculating
 303 the content in grams of metallic Al present in MIBA, after proper comparison with a control test
 304 using pure Al powder. 0.11 g of $\text{H}_2 \uparrow$ are expected to be produced per each gram of Al consumed.
 305 0.1 g of Al powder (control) or 10 g of MIBA were placed in an 800 ml solution of 2.5M NaOH
 306 and left to react for a period of 24 h. Three runs were performed; a displaced volume of $131.3 \pm$
 307 5.0 ml was observed per 0.1 g of Al powder. The temperature at which the reaction was carried out
 308 corresponded to 43 °C (exothermic reaction of NaOH in water). The density of the H_2 at 43 °C and

309 1 atm. pressure is 0.0766 kg/m³. From this property and the mass of H₂ produced by each gram of
 310 Al, it is possible to determine the theoretical volume of H₂ generated:

$$v = \frac{m}{\rho}; \quad v_{H_2} = \frac{0,11 \text{ g}}{0,0000766 \text{ g/ml}} = 1436,03 \text{ ml} \quad (6)$$

311 The results for MIBA showed 63.3 ± 1.2 ml of released H₂, corresponding to 43.65 mg of
 312 metallic Al in 10 g of MIBA. Therefore, there are around 4.36 g of metallic Al for each kg of
 313 MIBA, which corresponds to 6.3 L of released H₂↑ per kg of MIBA.

314 3.1.2 Aggregates

315 The particle size distributions and the results of apparent (ρ_a), rodded-dry (ρ_{rd}), saturated and
 316 surface-dried (ρ_{ssd}) and bulk (ρ_b) densities, and water absorption after 24 h (WA₂₄) for the two
 317 types of sand and RA are presented in Table 3. As expected, the density and water absorption of
 318 RA decreased and increased, respectively, in comparison with NA. Since the RA's particle size
 319 distribution was not equivalent to that of the combination of both fine and coarse sands, it was
 320 separated into different size fractions and subsequently combined in specific amounts. An addi-
 321 tional test was carried out to ascertain the water absorption dynamics of these aggregates over
 322 time, following Rodrigues et al. (2013), using a hydrostatic scale. After 10 minutes, the RA pre-
 323 sented a water absorption equivalent to 82% of that of its total capacity after 24 hours.

324 Table 3 - Physical properties of aggregates

Material	Fine sand	Coarse sand	Recycled aggregates	
Density (kg/m ³)	ρ _a	2652	2636	2510
	ρ _{rd}	2624	2601	2040
	ρ _{ssd}	2634	2614	2230
	ρ _b	1544	1556	1217
	WA ₂₄ (%)	0.40	0.51	9.33
Amount of material passing (%) in sieve (mm)	8.00	100	100	100
	4.00	100	96.6	100
	2.00	99.9	84.5	77.2
	1.00	98.9	42.6	42.3
	0.50	67.4	10.2	21.3
	0.250	9.5	3.3	8.3
	0.125	0.7	0.8	3.1
	0.063	0.3	0.3	1.8

325

326 **3.2 Fresh state performance of mortars**

327 **3.2.1 Consistence**

328 A consistence range of 170 ± 25 mm was adopted for all mixes to provide sufficient workability
329 and stability. However, the reference mix using cement exhibited a spread of 223 mm. Neverthe-
330 less, these specimens are meant to provide an example of changing properties for equivalent mix
331 design, but without direct comparison since the specimens were made using different methods and
332 placed in changing curing conditions. For MIBA mixes with NA, the mixing methodology con-
333 sisted of waiting 1 hour after the beginning of the procedure, so that a considerable portion of the
334 reaction of metallic Al would take place, thereby avoiding the entrapment of most of the H_2 gas in
335 the mix. Also, it should be noted that FA-containing mixes were produced with a liquid/binder ratio
336 of 0.5, whereas that of MIBA-based mixes was equal to 0.65. Despite the efforts to maintain equiv-
337 alent ratios with the use of a considerable amount of water-reducing admixtures of different types,
338 alkali-activated MIBA mortars presented considerable water requirement and were unworkable at
339 lower liquid/binder ratios. From this stage forward, even though FA- and MIBA-based mortars are
340 presented in parallel, a direct comparison of results is not possible since they have different mix
341 designs and thus varying porous microstructures. FA-NA mixes exhibited a slump flow of 185
342 mm, which decreased to 152 mm with the incorporation of RA. BA-NA and BA-RA mixes pre-
343 sented values of 173 mm and 164 mm, respectively. For both binders, the incorporation of RA
344 induced, as expected, a less workable paste. Since the water absorption of RA was compensated
345 by an additional amount of water, this decreased workability may likely have been due to the an-
346 gularity of RA, relatively to NA, which resulted in a greater internal interparticle friction.

347 **3.2.2 Fresh density**

348 The control cement mortar presented a fresh-state density of 2248 g/dm^3 . FA-NA and FA-RA
349 mixes exhibited densities of 2260 g/dm^3 and 1970 g/dm^3 , respectively, showing an expected

350 decrease with the incorporation of RA. These values were 1901 g/dm³ and 1744 g/dm³, for BA-
351 NA and BA-RA, respectively. To understand the effect of the metallic Al reaction with the
352 NaOH solution and the consequent H₂ entrapped in the mix (Figure 4), this test was made 1 h
353 after the first test for BA-NA mixes; the fresh density increased to 2004 g/dm³, corresponding
354 to a 5% increase when compared to the lighter sample measured after 15 min of mixing, thus
355 showing a considerable release of entrapped H₂ gas during that time.



356

Figure 4 - H₂ gas formation in the preparation of mortars

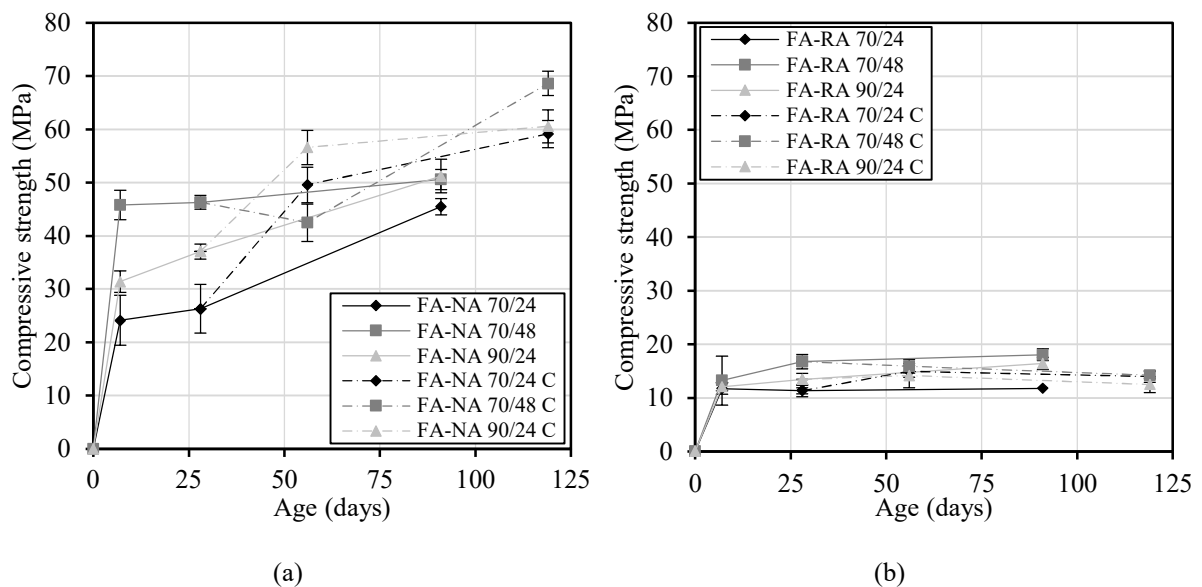
357

358 3.3 Hardened state performance of mortars

359 3.3.1 Compressive and flexural strength

360 The compressive strength of the control cement mortars after 7, 28 and 91 days were 43.9 MPa,
361 55.2 MPa and 66.2 MPa, respectively. Figure 5 presents the results of the compressive strength
362 over time for alkali-activated FA specimens exposed to different curing regimens. The trend for
363 FA mixes is in line with that observed by previous researchers (Atiş et al., 2015), in which higher
364 initial strength was observed for mixes exposed to a longer thermal curing period. In this case,
365 70/48 mixes presented higher initial strength, followed by 90/24 and 70/24. This implies that, after
366 a given temperature, the introduction of a higher amount of total energy (temperature × time)

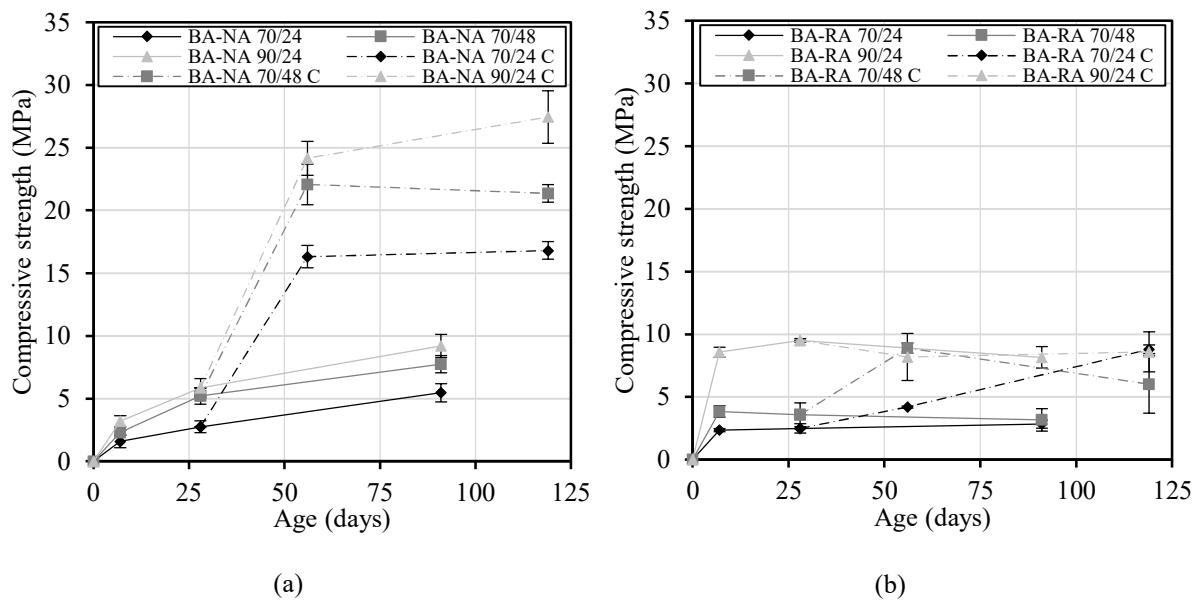
367 (Elyamany et al., 2018) catalyses the nucleation of aluminosilicate particles with subsequent
 368 growth of zeolite-like structures (Duxson et al., 2007). However, over time, 70/24 and 90/24 FA-
 369 NA mixes showed greater strength development during the 91 days inferring continuous reactions
 370 of condensation-crystallization showing considerable interest from an energy-saving perspective.



371 Figure 5 - Compressive strength of alkali-activated FA containing (a) NA and (b) RA (C - carbonated)
 372 Concerning FA-RA mixes (Figure 5b), the first trend was also observed, in which higher initial
 373 strength was presented by mixes exposed to a higher amount of energy, even though little strength
 374 development was observed after 28 days. A comparison of the compressive strength of FA-NA
 375 and FA-RA mixes shows that there was a loss of 57-64% after fully replacing the NA fraction. This
 376 level of strength loss was also observed in the study of Shi et al. (2012), wherein the incorporation
 377 of 100% coarse RA resulted in a mere strength loss of 10% in the cement-based concrete, whereas
 378 the same replacement level in FA-activated concrete led to a decrease of about 36%. Although
 379 some strength loss is expected with the incorporation of RA, the magnitude observed in this study
 380 and others (Shi et al., 2012) is greater than that typically observed in conventional cement-based
 381 mixes (Silva et al., 2014a). Besides the obvious higher porosity of RA relative to NA, this strength
 382 loss may have been due to partial adsorption of Na^+ and OH^- ions from the alkaline solution by the
 383 RA, thereby decreasing the total amount available to react with the binder. Consequently, these

384 ions may have catalysed an alkali-silica reaction of the RA, possibly leading to internal expansion
 385 and subsequent cracking. This aspect needs to be further analysed in future studies.

386 MIBA-containing mixes exposed to a 90/24 regime presented higher initial strength and constant
 387 development over time until 91 days, followed by the 70/48 and 70/24 mixes (Figure 6). When RA
 388 were incorporated, a similar plateau in strength development was observed; comparable compres-
 389 sive strength was seen after 7 and 91 days, regardless of the curing regime. Since a constant strength
 390 increase would be expected from the continuous condensation-crystallization of the precursor (ob-
 391 served for both FA-NA and BA-RA), additional analysis is needed to ascertain the impact of RA
 392 on strength development. Furthermore, it should be noted the oil-based release agent showed de-
 393 creased efficacy when demoulding alkali-activated mortars (mostly those exposed to a 90/24 cur-
 394 ing), which resulted in the detachment of part of the material. Additional analysis should be carried
 395 out to ascertain the compatibility of release agents for alkali-activated materials.

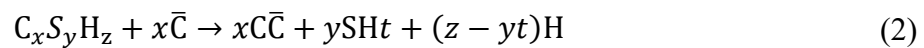


396 Figure 6 - Compressive strength of alkali-activated MIBA containing (a) NA and (b) RA (C - carbonated)
 397 Even though a direct comparison is not possible between FA and MIBA mixes since they were
 398 made with different mix designs, the strength development of the latter was markedly lower con-
 399 sidering the increase in liquid/binder ratio. The decreased strength is due to the aforementioned

400 reaction of metallic Al with NaOH, leading to considerable entrapped H₂ gas, which naturally
401 affected the macrostructural performance of the specimens. Furthermore, the Chapelle test sug-
402 gests that MIBA contains a smaller portion of amorphous silica and alumina when compared to
403 FA, which naturally means that it is a less reactive material.

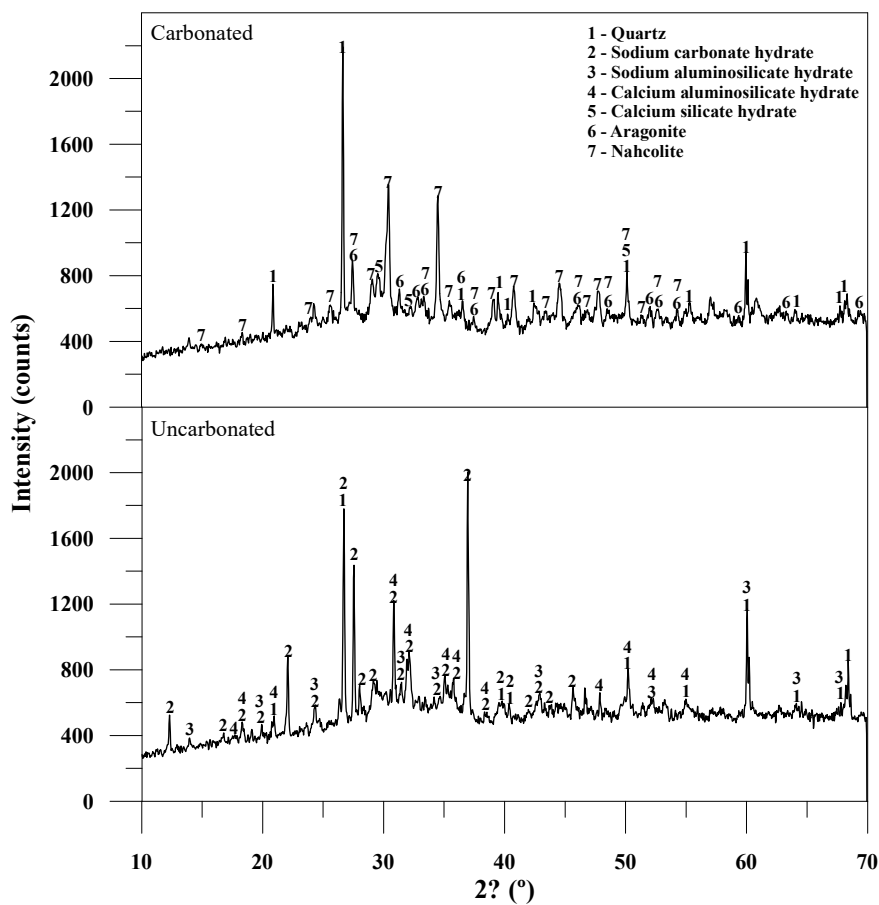
404 A resistance to carbonation test was initially envisaged at the beginning of this experimental cam-
405 paign to understand the velocity of pH level decrease as the specimens were exposed to CO₂ gas.
406 However, the test results were inconclusive since all specimens were carbonated after just 28 days
407 (i.e. none of the alkali activated materials presented a pinkish hue), whereas the control cement
408 mortars presented depths 3.7 mm and 4.4 mm after 28 and 91 days, respectively. A faster pH de-
409 crease due to carbonation was expected since AAM do not usually have Ca(OH)₂ available to car-
410 bonate (Palacios and Puertas, 2006) and the amount of OH⁻ ions, from the NaOH solution, de-
411 creases over time as they react with Si and Al species in the destruction-coagulation process (Provis
412 and van Deventer, 2014). Nevertheless, all specimens intended for carbonation testing were sub-
413 jected to flexural and compressive strength testing to ascertain the effect of carbonation on the
414 mechanical performance of these mortars. Figure 5 and Figure 6 also present the strength develop-
415 ment over time of the same mixes. Until the age of 28 days, all specimens were subjected to the
416 same curing environment and then exposed to a CO₂-rich environment for 28 days and 91 days
417 (total age of 56 days and 112 days, respectively). Within those 28 and 91 days in the carbonation
418 chamber, a clear strength increase was observed. When compared with the specimens exposed to
419 28 days of normal curing in an environmental chamber, strength increased about 20 MPa for FA-
420 NA 70/24 and 90/24. For unknown reasons, this was not observed for FA-NA 70/48, which pre-
421 sented strength reduction after 28 days, even though it showed nearly 70 MPa after 91 days (control
422 cement mortar presented a 91-day compressive strength of 69.2 MPa). All 112-day carbonated
423 mixes showed strength gain between 18% and 36% when compared with 91-day uncarbonated
424 ones. A more prominent strength gain was observed in BA-NA mixes (Figure 6a), with increases

425 of 275% to 306% (equivalent to absolute variations between 11 MPa and 18 MPa), wherein the
 426 BA-NA 90/24 presented a compressive strength of about 28 MPa after 91 days of carbonation.
 427 This considerable strength gain in both FA-NA and BA-NA mixes first starts with the dissolution
 428 of CO₂ into carbonic acid (H₂CO₃), decreasing pH level locally, which subsequently led to decom-
 429 position of e.g. alkaline metal-based compounds, Ca(OH)₂, silicates and aluminates in the matrix.
 430 In the case of Ca-bearing compounds (mostly for MIBA-based mortars), a decalcification followed
 431 by precipitation of calcium carbonate polymorphs (CaCO₃ in the form of vaterite, aragonite or
 432 calcite) and polymerization process of amorphous SiO₂ (see equation 1 and 2, where CH - Ca(OH)₂,
 433 C - CaO, \bar{C} - CO₂, S - SiO₂, H - H₂O) (Morandea et al., 2014).



434 Ca²⁺ ions, from the decalcification process, tend to migrate and precipitate in the form of CaCO₃
 435 in adjacent interstitial spaces thereby increasing the density of the matrix, which ultimately re-
 436 sults in enhanced mechanical performance. Additionally, the SiO₂ gel is also likely to have a
 437 predominant role in the overall strength increase of the microstructure, since the Si-O bonds of
 438 the Q³ and Q⁴ SiO₄ tetrahedra have a considerable bond strength (Li et al., 2018). Even though
 439 AAM based on class F FA are likely to present low content of Ca-bearing phases due to the low
 440 CaO content of the precursor (i.e. ~4.5%), they contain C-(N-)A-S-H, which may decalcify and
 441 lead to the formation of CaCO₃ and silica gel. The N-A-S-H gel is considered to be stable with
 442 ensuing diffusion of CO₂ in the microstructure. Therefore, it is likely that the strength increase
 443 of FA-based specimens occurred due to formation of carbonation products from the reaction of
 444 Na⁺ and Ca²⁺ ions in the pore aqueous solution into sodium bicarbonate (Nahcolite - NaHCO₃)
 445 and gaylusite (Na₂Ca(CO₃)₂·5H₂O). Since this led to the depletion of cations available to preserve
 446 the equilibrium of the metastable N-A-S-H gel, neighbouring groups Si-OH, Si-ONa, Al-OH or
 447 Al-ONa condense and merge to Si-O-Si or Si-O-Al gels thereby increasing the degree of

448 polymerization (Nedeljković et al., 2018). Indeed, looking at the results of the XRD analysis of
 449 carbonated and uncarbonated pastes equivalent to BA-NA 70/24 mixes (Figure 7), the XRD
 450 spectrum of the uncarbonated mix demonstrated the occurrence of polymerization reactions cor-
 451 roborated by the presence of hydrated sodium aluminosilicate ($\text{Na}_6[\text{AlSiO}_4]_6 \cdot 4\text{H}_2\text{O}$). Hydrated
 452 sodium carbonate ($\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$) was also identified, as well as crystalline SiO_2 , which came
 453 from the unreacted precursor and is present in all samples. The carbonated paste contained cal-
 454 cium silicate hydrate ($\text{Ca}_{1.5}\text{SiO}_{3.5} \cdot x\text{H}_2\text{O}$) or C-S-H, aragonite (CaCO_3) and nahcolite (NaHCO_3).

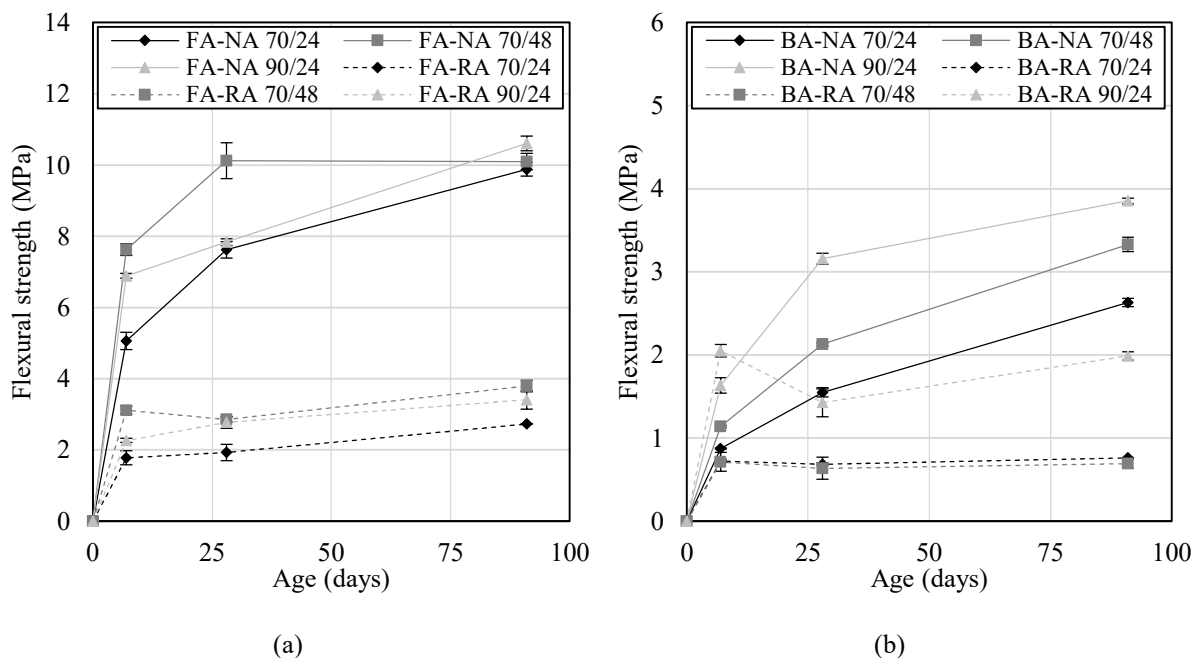


455
 456 Figure 7 - XRD spectrum of carbonated and uncarbonated BA-NA 70/24

457 Concerning FA-RA and BA-RA mixes, although a strength gain was also expected with ensuing
 458 carbonation since RA have higher content of Ca-bearing phases than NA, equivalent or slightly
 459 enhanced performance was observed. This can be explained by the likely inexistence of $\text{Ca}(\text{OH})_2$
 460 in the RA's adhered mortar, which would have been almost entirely carbonated before its use

461 (Gonçalves et al., 2020). Also, in another experimental campaign, carried out in parallel to this one,
 462 almost all carbonated specimens exhibited strength loss from 28 to 91 days, despite an initial in-
 463 crease in the first 28 days. The carbonation process may have generated tensions around unreacted
 464 particles in carbonated areas due to carbonation-induced shrinkage. This phenomenon, in combi-
 465 nation with increased shrinkage of mixes with RA, may have caused extensive micro-cracking
 466 thereby leading to strength loss after long exposure to a CO₂-rich environment (Bernal et al., 2013).

467 Regarding the results of the flexural strength test, the control cement mortars presented values
 468 of 5.3 MPa, 6.9 MPa and 6.8 MPa after 7, 28 and 91 days, respectively. AAM based on FA
 469 demonstrate slow strength development during the first 28 days, due to the slow polymerization
 470 reactions over time (Olivia and Nikraz, 2012). However, enhanced flexural strength can be
 471 seen after 28 days and 91 days (Figure 8), because of the physical strength of the three-dimen-
 472 sional structure as a result of the polymerization reactions.

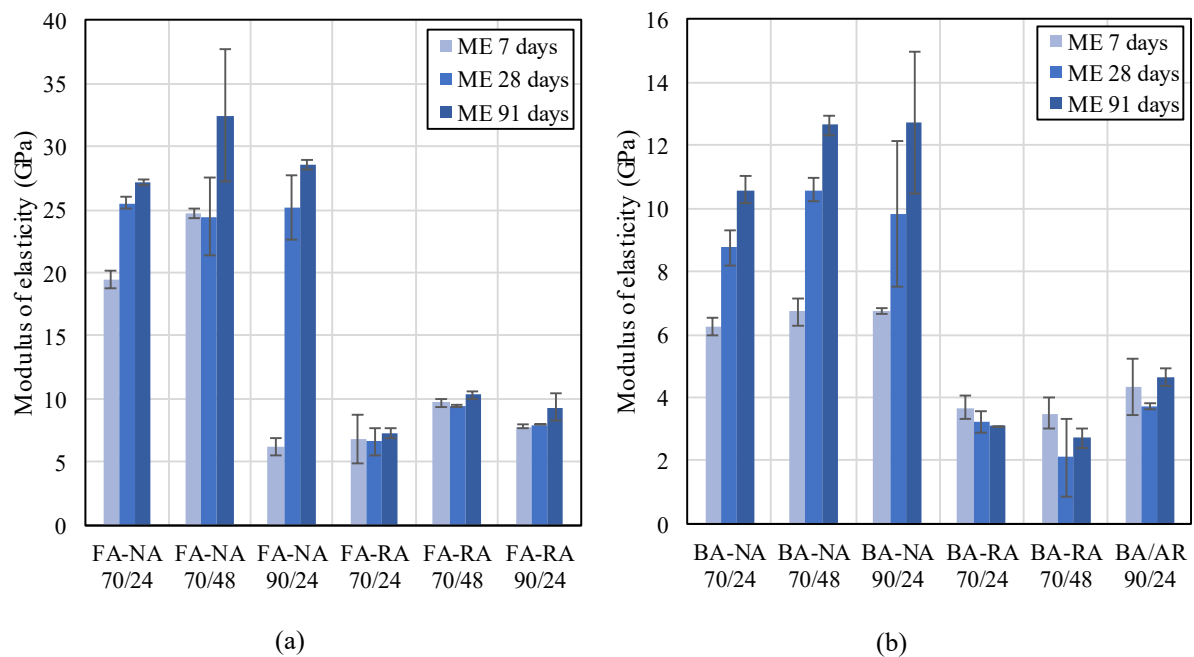


473 Figure 8 - Flexural strength of (a) FA and (b) MIBA mixes
 474 Alkali activated FA mixes showed considerably higher values. The results of the flexural strength
 475 test showed a similar trend to that of the compressive strength; in FA-NA mixes, higher strength

476 was achieved by those cured in 70/48 conditions, followed, by 90/24 and 70/24, the difference
 477 between which was offset until 91 days. This suggests that, even though the 70/48 curing condi-
 478 tion could be deemed the optimum regime to provide higher initial strength, in the light of the
 479 equivalent performance after 91 days, 70/24 could be considered more environmental-friendly
 480 for a given target behaviour. The incorporation of RA led to considerable strength decrease (i.e.
 481 loss of about 65% between FA-RA and FA-NA mixes). Again, even though this trend was ex-
 482 pected, the incorporation of RA does not usually lead to such losses (Silva et al., 2015). Alkali
 483 activated MIBA mixes showed decreased performance due to the corrosion reactions of metallic
 484 Al and the lower amount of reactive phase. Nevertheless, a steady increase in flexural strength
 485 can be seen even after 91 days, similar to those of the compressive strength.

486 3.3.2 Modulus of elasticity

487 The control cement mixes presented dynamic moduli of elasticity of 35.6 GPa, 38.4 GPa and 40.7
 488 GPa after 7, 28 and 91 days, respectively. Figure 9 presents the results of the dynamic modulus of
 489 elasticity test for alkali-activated FA and MIBA mixes.



490 Figure 9 - Dynamic modulus of elasticity of (a) FA and (b) MIBA mixes

491 Regardless of the curing condition, FA-NA mixes showed about 35% lower moduli of elasticity
 492 when compared to the 28-day value of the control cement mix. As expected, FA and MIBA spec-
 493 imens subjected to a 70/48 curing presented higher moduli of elasticity in comparison with those
 494 from 90/24 and 70/24 regimens. An immediately perceivable difference can be seen between
 495 mixes with and without RA; its incorporation led to a decrease of around 70%. Although a
 496 notable decrease would be expected as RA demonstrate greater deformability in comparison
 497 with NA, the magnitude is higher than that typically observed for conventional cement-based
 498 mixes (Silva et al., 2016). Also, whilst FA-NA and BA-NA mixes presented a continuous in-
 499 crease over time, those with RA plateaued after 7 days.

500 3.3.3 Ultrasonic pulse velocity

501 Table 4 shows the results of the ultrasonic pulse velocity test. For two of the specimens (i.e. 7-day
 502 FA-NA 70/24 and 28-day BA-NA 70/48), the test was not possible due to irregular surfaces and
 503 loss of material, making them unrepresentative. None of the 91-day values was measured due to
 504 technical difficulties of the equipment. The results can be well correlated with those of the dynamic
 505 moduli of elasticity. Again, 70/48 curing provided initially increased densification leading to higher
 506 moduli of elasticity with progressively lower difference until 91 days. As expected, all samples
 507 made with RA had lower results when compared with the control NA mixes. The results of the
 508 control cement mortars were 4126 m/s, 4586 m/s and 4565 m/s after 7, 28 and 91 days, respectively.

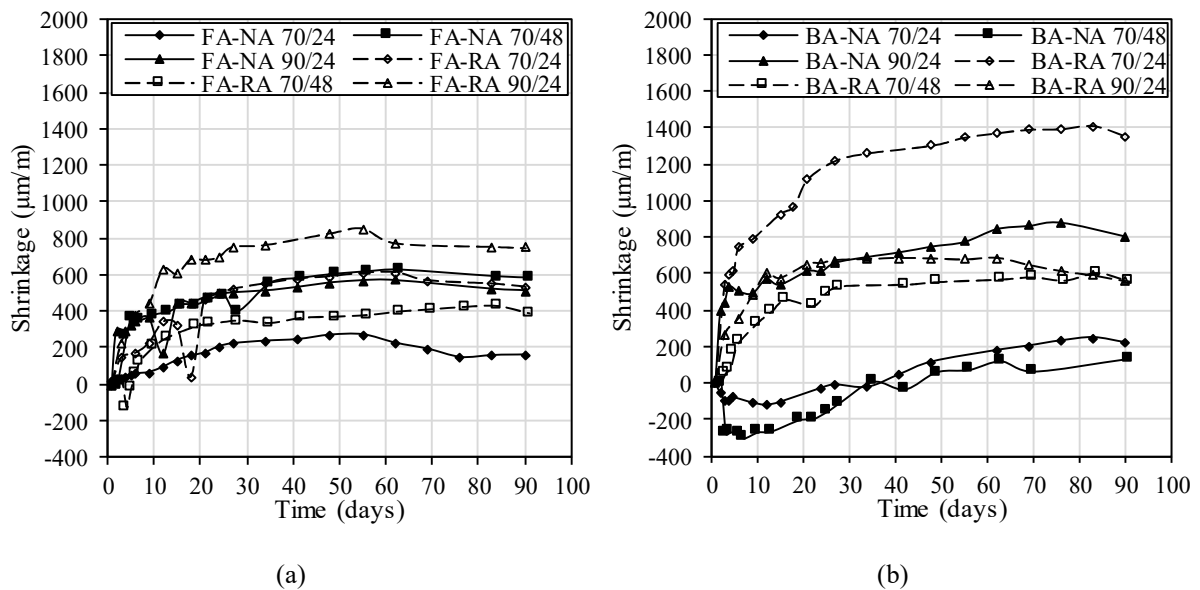
509 Table 4 - Ultrasonic pulse velocity of FA and MIBA mixes

Mix	Ultrasonic pulse velocity (m/s)			
	7 days	28 days	91 days	
FA-NA	70/24	-	3613	3584
	70/48	3597	3743	3813
	90/24	2939	2632	3756
FA-RA	70/24	2341	1755	2439
	70/48	2521	2181	2561
	90/24	2132	2127	1972
BA-NA	70/24	1982	2183	-
	70/48	2830	-	-
	90/24	2068	2379	-
BA-RA	70/24	1623	1590	-
	70/48	1543	1860	-
	90/24	2362	2147	-

510

511 **3.3.4 Shrinkage**

512 Figure 10 presents the dimensional variation over time of the alkali-activated mixes. An initial
 513 analysis of the results of the FA and MIBA mixes shows that there was a greater dispersion of the
 514 latter with changing curing conditions and incorporation of RA. FA-NA 70/24 was considered as
 515 the most stable material with the least variation over time ($\sim 200 \mu\text{m/m}$ after 91 days). FA-NA 70/48
 516 and 90/24 showed equivalent performance and a final shrinkage strain (i.e. $500\text{-}600 \mu\text{m/m}$) equiv-
 517 alent to that expected from typical cement mortars (Gonçalves et al., 2019). As expected, due to
 518 the greater deformability of RA (Silva et al., 2014b), the incorporation of RA led to higher shrink-
 519 age strain. However, it should be noted that unusual isolated expansion phenomena occurred in
 520 these specimens at certain ages (Figure 10a), which may indicate changing conditions of the curing
 521 environment. This may have resulted in lower than expected final shrinkage strains.



522 Figure 10 - Dimensional stability of alkali-activated (a) FA and (b) MIBA mixes

523 Although BA mixes were expected to present greater shrinkage due to the lower content of
 524 amorphous phases and formation of H_2 gas, most of them showed the equivalent performance
 525 of FA mixes. The BA-RA 70/24 mix presented notably higher shrinkage strain ($\sim 1400 \mu\text{m/m}$)
 526 when compared with that of the BA-RA 70/48 and 90/24 mixes ($\sim 600 \mu\text{m/m}$). However, this

527 discrepancy was observed in BA-NA 90/24, which presented a final shrinkage strain of about
528 800 $\mu\text{m}/\text{m}$. Additionally, BA-NA 70/24 and 70/48 showed considerable expansion in the first
529 3-5 days of curing and started to shrink after that. The expansion may have been due to the
530 formation of H_2 gas from the reaction of metallic Al, which did not corrode entirely in the
531 thermal curing process due to the lower temperature input. However, since this trend was not
532 observed in BA-RA mixes, additional testing is required to comprehend the effect of both
533 MIBA activation and RA incorporation on this property.

534 **3.3.5 Water absorption by capillary action**

535 Figure 11 presents the water absorption by means of capillary action of FA mixes. Although
536 this test was also carried out on BA mixes, because of a change in the water's colour (brownish
537 hue) and considerable efflorescence and mass loss of the specimens, the results would not be
538 representative of the property and were thus discarded. Although FA-NA 70/24 presented the
539 lowest sorptivity over time, little difference was observed for mixes exposed to different curing
540 regimen. As expected from mixes containing RA and similar to the results of Nuaklong et al.
541 (2016), the incorporation of RA led to greater internal porosity and pore interconnectivity,
542 thereby leading to higher water absorption by capillary action. A more expected trend was
543 observed specimens containing RA regarding the effect of the thermal curing regime; FA-RA
544 70/48 and 70/24 presented the lowest and highest values respectively, which can be well cor-
545 related with the results of the compressive and flexural strength tests as well as those of the
546 dynamic moduli of elasticity. The control cement mortar showed a mass gain per unit area of
547 about $12 \times 10^{-3} \text{ g}/\text{mm}^2$ after 72 hours, being almost twice more than that of FA-NA mixes with
548 equivalent mix design. This infers that the alkali activation of FA is capable of producing a
549 more tortuous and less interconnected porous network (Shi et al., 2012).

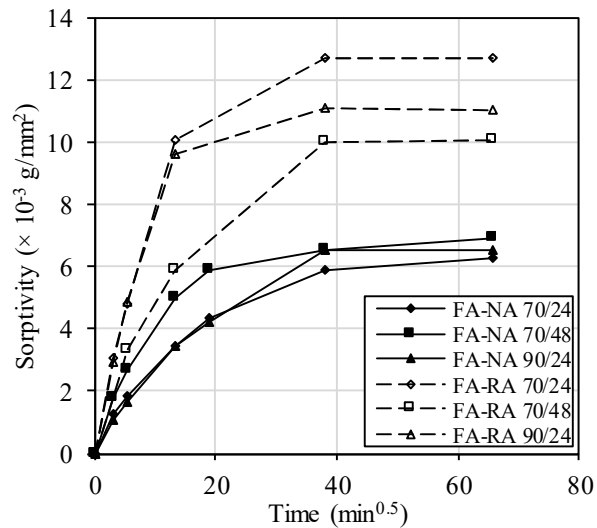


Figure 11 - Water absorption by capillary action of FA mixes

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Concerning the poor physical stability of the MIBA-based mortars when exposed to the test, leaching of constituents was observed, which led to a brownish colour of the test water, probably due to leached ferrous compounds. Because of the environmental impacts of this phenomenon, an upcoming experimental campaign on the leaching behaviour of alkali-activated MIBA-based mortars is expected to be carried out in the near future within the scope of the research project PTDC/ECI-CON/29196/2017 (RInoPolyCrete). Ferrous compounds, apart from not dissolving in an alkaline environment, can form bonds with Al in a spinel system or with iron-rich glasses, decreasing the available amount of Al and Si for the polymerization reactions thereby leading to decreased strength (Chen-Tan et al., 2009) and the possibly greater likelihood of being leached. The precipitated material, resulting from the evaporation of water from each test, was analysed by XRD to understand the nature of the leached compounds from BA-NA specimens (Figure 12). It mostly contained sodium carbonates (in the form of thermonatrite - $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ - ICDD # 001-1015 and trona - $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ - ICDD # 029-1447) and halite (NaCl - ICDD # 001-0994). These results suggest a considerable amount of Na^+ ions in the solution, which did not partake in the reaction with the precursor (Criado et al., 2005; Provis and van Deventer, 2014), leached into the test water and reacted directly with atmospheric CO_2 .

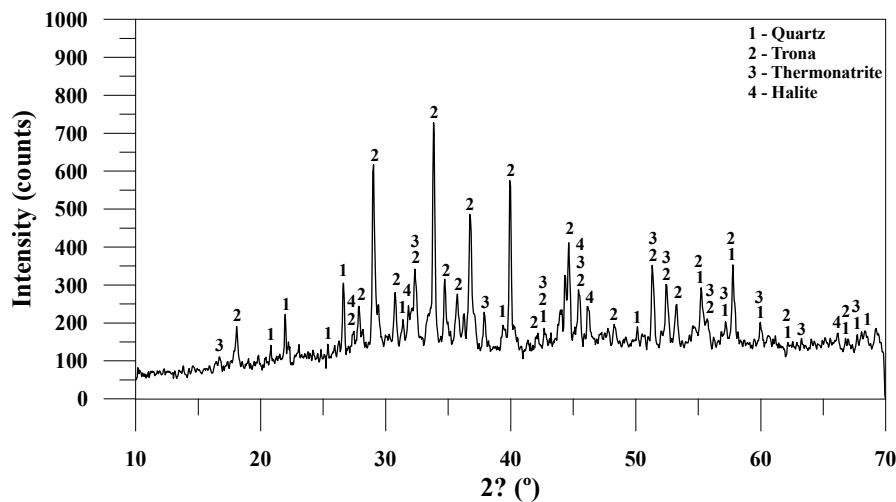


Figure 12 - XRD analysis of efflorescence precipitates from BA-NA specimens

568

569

570 4 Conclusions

571 The effect of RA on the mechanical and durability-related performance of alkali-activated FA
 572 and MIBA mixes was evaluated. MIBA has a similar chemical composition to that expected from
 573 class C FA. However, it is comprised of a lower quantity of amorphous material (primarily from
 574 waste glass), thereby presenting poorer reactivity in an alkaline medium when compared to FA.

575 Additionally, MIBA contains a considerable amount of ferrous metals that could be further ex-
 576 tracted at the treatment facility. Still, since the electromagnetic separation of non-ferrous metals
 577 through Eddy current is not very effective, metallic Al is always likely to be present in MIBA.

578 As a result, it will react with the OH⁻ ions from the NaOH solution causing the formation of H₂
 579 gas, which becomes entrapped in the fresh mix. Furthermore, after the thermal curing process,
 580 which catalyses this reaction and promotes setting, excessive expansion and internal porosity is
 581 likely to be observed. This higher porosity, in combination with the lower reactivity of MIBA,

582 leads to a considerable decline in performance. However, notable performance enhancement can
 583 be observed in specimens exposed to accelerated carbonation. This occurs as a result of the de-
 584 calcification of Ca-bearing phases and consequent precipitation of CaCO₃ polymorphs, as well

585 as from the carbonation of Na⁺ in the pore solution into sodium carbonates, both of which in-
 586 crease the degree of polymerization of Si-O-Si and Si-O-Al gels, thereby significantly increasing

587 the material's strength. The incorporation of RA, as expected, led to an overall decline in perfor-
588 mance, but its magnitude was greater than that typically observed by conventional cement-based
589 concrete and mortar. This infers the presence of an underlying nefarious phenomenon, possibly
590 the extensive micro-cracking due to alkali-silica reaction of RA with the alkaline activator, which
591 requires further evaluation in upcoming experimental campaigns.

592 **Acknowledgements**

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599 **Data availability**

600 The raw/processed data required to reproduce these findings cannot be shared at this time as
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