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Advances, Issues, and Perspectives**

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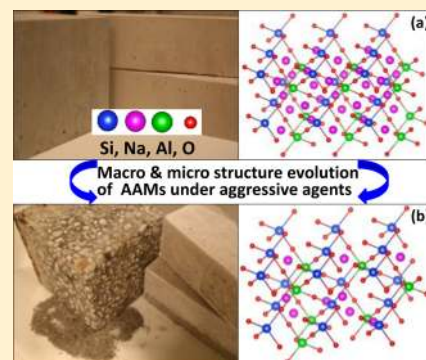
1 A Review on the Durability of Alkali-Activated Fly Ash/Slag Systems: 2 Advances, Issues, and Perspectives

3 Kamel Arbi,* Marija Nedeljkovic, Yibing Zuo, and Guang Ye

4 Materials & Environment (Microlab), Faculty of Civil Engineering and Geosciences, Delft University of Technology, Delft, The
5 Netherlands

6 **S** Supporting Information

7 **ABSTRACT:** Alkali-activated materials (AAMs) have high potential as alternative
8 binder to ordinary portland cement (OPC), because of their high performance
9 beside lower CO₂ emissions. While there is a general consensus about their strength
10 advantages over OPC, there is a widespread debate regarding their durability. Some
11 groups believe that the availability of wide scientific/technical background, together
12 with the already-known OPC durability problems, are sufficient for their
13 commercialization; however, others consider the durability of AAMs to be an
14 unproven issue. This controversy represents one of the limitations facing their bulk
15 applications. The present work provides an overview of the latest developments on
16 durability of fly ash/slag-based AAMs with the aim to update recent findings
17 regarding their behavior under aggressive conditions (sulfates, freeze–thaw, chloride,
18 carbonation, acid, efflorescence). This review will provide a better understanding of
19 the durability issues of AAMs, which will stimulate further research to develop the
20 appropriate testing methods and help to promote their commercialization.



1. INTRODUCTION

21 Cement and concrete are central to modern civilization, with its
22 reliance on the built environment to provide a high quality of
23 life. Next to water, concrete is the most consumed substance on
24 the planet and is produced in volumes exceeding 10 billion tons
25 per year worldwide.^{1–3} Ordinary portland cement (OPC)-
26 based concrete is still the material of choice and the most
27 widely used in construction and civil engineering, because of
28 the ease of use and generally good performance, including
29 excellent thermal and mechanical properties, besides offering an
30 average life cycle of more than 100 years.

31 However, with the current focus on environmental issues, the
32 cement industry causes serious destruction of natural quarries
33 through the extraction of raw materials. It also contributes ~8%
34 of global CO₂ emissions^{3–5} and consumes more than 10% of
35 the total energy used.^{6,7} The total emissions footprint of ~0.8–
36 0.9 t CO₂ per ton of OPC produced are mainly due to the
37 decomposition of limestone (0.53–0.55 t) and the combustion
38 of fossil fuels (0.34–0.39 t) during cement production.^{5,8–10}

39 After the 2009 Copenhagen climate summit, where the
40 international community agreed to keep global average
41 temperature increase below 2 °C, a more significant reduction
42 in CO₂ emissions (20%–50%) was strictly adopted by several
43 countries/continents to guarantee a “normal” human habit-
44 ability. In this context, the European Union has made a
45 unilateral commitment for 2020 to reduce overall greenhouse
46 gas emissions from its 28 member states by 20%, compared to
47 1990 levels. In the same way, China, as the world’s largest
48 emitter of CO₂, announced that, by 2020, its carbon dioxide
49 emissions per unit of gross domestic product (GDP) will be

reduced by 40%–45% from the 2005 level.^{11,12} Consequently,
50 the cement industry is under pressure to reduce both energy
51 use and greenhouse gas emissions and is actively seeking
52 alternatives to these serious concerns. The interest in reuse of
53 other industrial by products such as fly ash (FA) from coal
54 combustion, blast furnace slag (BFS) from iron production,
55 silica fume (SF) from ferrosilicon production, and rice husk ash
56 (RHA) from burning agricultural rice waste as supplementary
57 cementitious materials (SCMs) has been greatly increased and
58 new eco-efficient binders such as calcium aluminate
59 cements,^{13–16} calcium sulfoaluminate cements,^{17–21} super-
60 sulfated cements,^{22–24} and alkali-activated binders^{25–41} have
61 been developed. Among them, alkali-activated materials
62 (AAMs), and those classified as geopolymers,^{42,43} are a high-
63 profile example able to produce cement and concrete with the
64 advantages of OPC but with a large reduction in CO₂ emissions
65 and general aspects of good performances (high early strength,
66 good resistance against acid and sulfate attack, etc.). AAMs and
67 GPC have emerged as novel engineering materials with the
68 potential to form a substantial element of an environmentally
69 sustainable construction and building products industry.^{44–47}
70 AAMs are basically formed by aluminosilicate precursors, which
71 are generally, but not limited to, industrial byproducts such as
72 FA and BFS, aggregates, and activator. 73

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74 During the last few decades, AAMs and GPC have become
75 research targets for teams worldwide and numerous studies
76 have been conducted to determine the composition and
77 microstructure property relationships in such systems. While
78 chemical principles, reaction phenomena and engineering
79 properties of these materials have been reviewed exten-
80 sively;^{48–59} their durability with regard to testing methods
81 and protocols is scarcely discussed, and only a few documents
82 discussing their long-term performances could be found in the
83 literature.^{5,10,60–62}

84 This work presents up-to-date information on most relevant
85 advances in durability researches related to AAMs and GPC
86 systems during the last 10 years. Special attention has been paid
87 to durability tests including methodologies and protocols for
88 the analysis of this new generation of binders. The present
89 paper does not address all testing methods to predict life
90 service of these materials. Rather, we will limit our work to FA-
91 and BFS-based systems. These two industrial byproducts have
92 been reported as the most promising precursors for large-scale
93 industrial production of GPC, because of the more favorable
94 rheological properties and lower water demand achievable
95 when compared to mixes based on calcined clays. Concerning
96 durability testing methods, we have adopted almost the same
97 criteria of the RILEM TC 247-DTA Committee. On the one
98 hand, chloride and carbon dioxide penetration is associated
99 with the degradation of embedded steel reinforcement; on the
100 other hand, sulfate and freeze–thaw exposure evaluates the
101 stability of the binders. Acid and efflorescence resistances have
102 been also reviewed; however, the alkali–silica reaction is not
103 included in this work and a detailed analysis of this section
104 could be found in a recently published work.⁶²

105 The aim of the present review is to provide better
106 understanding of long-term performances and engineering
107 properties of these systems and also to stimulate further
108 research in this topic. Some issues related to testing
109 methodologies and future challenges are also raised in this
110 work.

2. DURABILITY

111 Concrete may deteriorate when exposed to aggressive environ-
112 ments. These deteriorations may be classified as physical,
113 resulting from exposure to extreme environmental changes such
114 as freeze/thaw or fire; chemical, being caused by acid or sulfate
115 attack, water, or the alkali–aggregate reaction; biological,
116 including the presence of bacteria; or structural, i.e., live loads
117 or load cycles. Relevant results published during past decade on
118 the latest trends on durability of alkali-activated fly ash and/or
119 slag focused on their resistance to sulfate attack, freeze–thaw
120 cycle, chloride ingress, carbon dioxide penetration, acid, and
121 efflorescence are reviewed in this work.

122 **2.1. Sulfate Resistance.** Sulfate attack is a complex damage
123 phenomenon caused by exposure of concrete products or
124 structures to an excessive amount of sulfate from internal (due
125 to sulfates present in the binder or aggregates) or external
126 sources (induced by the environment into which the concrete is
127 placed). Degradation of concrete exposed to sulfate salts is the
128 result of sulfate transport through the pore system, generation
129 of stresses due to the creation of expansive reaction products,
130 and the mechanical response (typically spalling and cracking) of
131 the bulk material due to these stresses.

132 A recent study on the evolution of alkali-activated fly ash/slag
133 (1:1 ratio) pastes exposed to sodium and magnesium sulfate
134 environments⁶³ have shown that the response to sulfate attack

is strongly dependent on the nature of the cation accompanying
the sulfate, rather than the sulfate itself. It has been reported
that immersion of geopolymer pastes in Na_2SO_4 does not lead
to any apparent degradation of the binder, and no conversion
of the binder phase components into sulfate-containing
precipitates was observable. These results have been attributed
to the fact that the geopolymer binder continues to stabilize
and develop in the presence of Na_2SO_4 (acting here as an
activator, rather than as an aggressive agent). However, MgSO_4
caused severe decalcification of the binder, formation of
gypsum, and loss of structural and dimensional integrity
(Figure 1). The authors also claimed that a distinction should

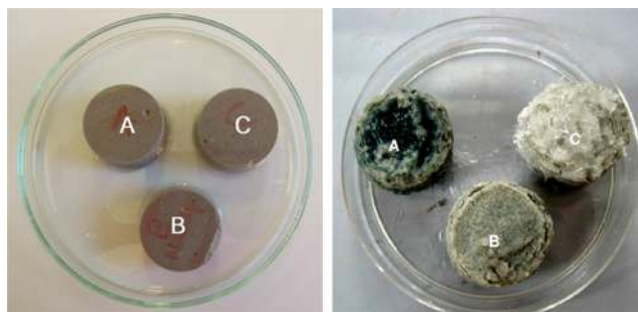


Figure 1. Fly ash/slag specimens aspect after immersion in Na_2SO_4 (left) and MgSO_4 (right) solution for 90 days: (A) w/b 0.40, (B) w/b 0.50, and (C) w/b 0.60. (Reproduced from ref 63. Copyright 2013, Springer, Dordrecht, The Netherlands.)

be drawn between “magnesium sulfate attack” (where both
 Mg^{2+} and SO_4^{2-} are capable of inducing damage in the
structure), and general processes related to the presence of
sulfate, accompanied by other, nondamaging cations.

Komljenovic et al.⁶⁴ studied the effects of external sulfate
attack (5% Na_2SO_4 solution) on mechanical and micro-
structural properties of alkali-activated slag (AAS), compared
with portland-slag cement (CEM II/A-S 42.5N). They
concluded that, after 90 days, AAS showed significantly higher
resistance to sulfate attack, with respect to the benchmark CEM
II, and attributed these findings to the absence of portlandite
and the unavailability of aluminum, substituted in C–S–H (I)
or present in hydrotalcite, for reaction with sulfates. These
results are in agreement with those reported previously,⁶⁵
where a comparative study between AAS and OPC concrete
exposed to 5% magnesium sulfate and 5% sodium sulfate
solutions during one year showed that the decrease on
compressive strength was ~17%–23% for AAS and ~25%–
37% for OPC-based concrete. Bakharev⁶⁶ investigated the
influence of activator (type, concentration, and the type of
cation in the sulfate media) on the stability of alkaline activated
fly-ash-based geopolymers. Two accelerating methods were
applied: (i) increased reaction surface (small specimens/large
surface areas) and (ii) increased concentrations of aggressive
agents. In addition, each of solutions was applied into three
different alkali-activation-based specimens and cured at 95 °C
for 24 h. The first group was activated with NaOH, the second
with Na_2SiO_3 , and the third one with a mixture of NaOH and
KOH. The best sulfate resistance in different sulfate solutions
was observed in NaOH-based geopolymers, because of the
stable cross-linked aluminosilicate polymer structure. More-
over, good resistance was linked to a refined pore structure as
the average pore size of the tested specimens prepared with
NaOH activator was minor. The compressive strength of the

181 samples was increased by 4%–12% over the exposure time. In
182 the case of specimens prepared using sodium silicate, the author
183 attributed the loss of strength to ettringite formation (observed
184 in the XRD patterns); however, we believe that the formation
185 probability of this phase in low-calcium systems such as FA-
186 based concrete is very low, making XRD results of this work
187 insufficient to confirm the presence of ettringite, taking into
188 account that, in sodium silicate FA samples, no deep cracks
189 have been detected in neither needle-shaped particles
190 (ettringite) were observed from SEM micrographs. The least
191 changes in specimens were found in the solution of 5% sodium
192 sulfate + 5% magnesium sulfate. The most significant
193 microstructural changes and strength fluctuations were
194 observed when 5% solutions of sodium sulfate and magnesium
195 sulfate are used. Diffusion of alkali ions into the solution caused
196 significant stresses and the formation of deep vertical cracks in
197 the specimens prepared using a mixture of NaOH and KOH.
198 Sulfate resistance of fly-ash-based geopolymer concrete from
199 blended ash of pulverized fuel ash and palm oil fuel ash has
200 been investigated⁶⁷ under 5% sodium sulfate exposure for a
201 period of 18 months and compared to that of OPC concrete
202 under the same exposure conditions. Changes in mass,
203 compressive strength, products of degradation, and micro-
204 structure have been evaluated in both systems. A better
205 resistance to sulfate attack in FA concrete, compared to that in
206 OPC, has been reported, which was attributed to low calcium
207 phases, low water demand, and compact microstructure in FA-
208 based concrete. Similar results have been reported in previous
209 work conducted on heat-cured fly-ash-based geopolymer
210 concrete after exposure to sodium sulfate solution for up to
211 one year.⁶⁸ However, none of these works^{67,68} explicitly
212 reported the important role of stable zeolites that are generally
213 formed in geopolymer systems, which can encapsulate sulfates
214 by preventing leaching. The formation of gypsum and then
215 ettringite in OPC concrete caused a reduction in compressive
216 strength, physical damage at the corners and edges of
217 specimens, and mass loss as the final deterioration indicator.
218 No significant changes in appearance have been detected after
219 18 months of immersion and only 4% of mass loss has been
220 found in geopolymer concrete. However, in OPC concrete,
221 more than 20% mass loss was reported, again indicating better
222 resistance of FA-based geopolymer systems. It has been also
223 reported⁶⁷ that compressive strength of geopolymer concrete
224 was increased by 7% and that of OPC decreased by 63% after
225 more than one year of exposure to 5% sodium sulfate solution.
226 The increase in compressive strength of geopolymer systems
227 also reported by Ismail et al.⁶³ and Bascarevic et al.⁶⁹ was
228 attributed to the fact that sodium sulfate is acting as an activator
229 rather than an aggressive agent, allowing the alkali activation
230 reaction to continue in the sulfate solution. However, from the
231 later work conducted in two different FA samples over a period
232 of 365 days,⁶⁹ a reduction in compressive strength of some
233 mixtures after sulfate treatment was reported. The same
234 authors⁶⁹ also reported that more-porous fly-ash-based geo-
235 polymer mortars demonstrated an increase in compressive
236 strength. This was in overall disagreement with the current
237 observation that a compact and denser microstructure displays
238 better mechanical, chemical, and physical properties. The
239 phenomenon was attributed to the prolonged geopolymeriza-
240 tion in sulfate solution favored by the presence of high amount
241 of alkalis. The authors emphasized that leaching is apparently
242 less affected by sulfate ions than by the high pH of the sulfate
243 solution. The initial pH value of Na₂SO₄ solution was 6, while

the final was reported to be ~12. Based on the theory, the main
244 degradation mechanism of aluminosilicate compounds at high
245 pH is the hydrolysis of the siloxane bonds induced by OH⁻
246 attack, which later causes desilication of the geopolymer matrix.
247 Consequently, Si⁴⁺ ions were leached, which was confirmed by
248 ²⁹Si MAS NMR analysis. The decreased Si/Al ratio was one
249 additional indicator of matrix degradation due to leaching of
250 Si⁴⁺. The authors attributed the higher observed leaching to the
251 higher pH of the sulfate solution. 252

From these results, it can be concluded that the relationship
253 between strength and sulfate treatment is still unclear and
254 requires deeper investigation in order to identify whether
255 sulfates improve or reduce the mechanical properties of these
256 binders. We believe that the curing conditions of reference
257 samples (laboratory conditions, fog room, immersed in tap
258 water, etc.) may have significant impact on their mechanical
259 properties and could explain the divergence trends reported on
260 compressive strength. In the case that sulfates positively affect
261 the durability of AAMs (by improving strength), should sodium
262 sulfate be considered as an aggressive agent in future
263 formulations of appropriate standards for durability testing of
264 these systems? 265

Through the review of different studies conducted in sulfate
266 resistance of slag and/or fly-ash-based AAM, it can be
267 concluded that this phenomenon is mainly affected by the
268 type of cation accompanying the sulfate, although durability can
269 also be influenced by other factors, such as precursors chemical
270 composition, calcium/magnesium content, the exposure
271 conditions, and even sample preparation and curing con-
272 ditions.^{5,63,69–71} 273

2.2. Freeze–Thaw Resistance. Freeze–thaw resistance is
274 dependent on the critical saturation point and the pore
275 structure of the concrete. When the critical saturation point is
276 achieved, unbound water freezes. The ice that is produced
277 occupies 9% more volume than that of water. If there is no
278 space for this volume, a hydraulic pressure is induced on the
279 pore wall surfaces, resulting in the cracking of material. In
280 addition, the freezing temperature of the pore solution is very
281 important. This point differs between geopolymer- and OPC-
282 based concretes, because of differences in ionic strength and
283 also differences in the critical pore radius confining the pore
284 fluids.⁵ 285

Glukhovskiy and Krivenko^{72–75} investigated the influence of
286 different alkaline activator solutions on freeze–thaw resistance.
287 It has been reported that sodium silicate-activated slag concrete
288 exhibited the greatest resistance, because of its less porous
289 structure. AAS concretes can bear 300–1300 cycles of repeated
290 freezing–thawing cycles, compared to the <300 cycles in the
291 case of OPC concrete. The influence of slag basicity on the
292 frost resistance has been also investigated, and it has been
293 found that the worst performance corresponds to acidic slag. 294

The freeze–thaw resistance of AAS-based concrete has been
295 investigated by Fu et al.,⁷⁶ where an accelerated freeze–thaw
296 cycling method was applied. The dynamic elasticity modulus
297 was measured every 25 cycles, up to 300 cycles. The authors
298 established two freeze–thaw cycle damage models, based on
299 experimental results: dynamic elasticity modulus attenuation
300 model and an accumulative freeze–thaw damage model. Each
301 one was designed with respect to damage variables. Two
302 functions were used to describe these damage models: power
303 function and exponential function. Functional equations were
304 established based on a dynamic elasticity modulus attenuation
305 model in the literature, and power function models were 306

307 superior to exponential function models with better precision
308 and relativity. By means of these models, the resistance of AAS
309 concrete to freeze–thaw cycling was evaluated. It was shown
310 that the weight loss decreased slightly, below 1% at 300 cycles.
311 The interpreted results showed significant freeze–thaw
312 resistance of AAS concrete (frost resisting grade above F300
313 and coefficient freeze–thaw resistance of ~90%), making it a
314 suitable candidate to be used in cold areas. Properties such as
315 low Ca/Si ratio, short original three-dimensional (3D)
316 structure, and better cushion power than that of C-S-H in
317 OPC concrete are observed, which benefits the corrosion
318 resistance of materials.^{26,76} The close-grained hydration
319 products make the structure of AAS concrete more compact,
320 which makes it difficult for water to penetrate and difficult for
321 concrete to become frozen and saturated, which makes AAS
322 concrete more durable.

323 Cai et al.⁷⁷ used response surface methodology (RSM) to
324 analyze the effects and interaction among three relevant
325 parameters on the freeze–thaw resistance of AAS concrete:
326 solution/slag ratio, slag content, and sand content. The most
327 important factor influencing the freeze–thaw resistance of AAS
328 concrete is the air-void structure. The freeze–thaw resistance
329 has a tendency to improve with a smaller air bubble space
330 coefficient and a bigger specific surface area. It has been also
331 found that the lower solution/slag ratios and higher slag
332 content in the mixture design exhibit the best freeze–thaw
333 resistance, while the sand content was found to have a minor
334 effect on the durability.

335 Škvára et al.⁷⁸ investigated the resistance of fly-ash-based
336 geopolymer mortar specimens to alternating freezing and
337 defrosting cycles, according to Czech Standard CSN 72 2452.
338 Samples with dimensions of 40 mm × 40 mm × 160 mm were
339 cured under laboratory conditions at ambient temperature and
340 40% relative humidity (RH) for 28 days before freeze–thaw
341 testing. Seven mixture designs were made, adding various
342 materials, such as OPC, limestone (in ground or aggregate
343 form), and three different air entraining agents. Geopolymer
344 samples were kept under water for 150 freezing and defrosting
345 cycles. Samples were broken after 28 days, 6 months, and 1
346 year, respectively. No bulk disintegration was observed, and no
347 mass loss of samples was observed. The compressive strength
348 values of samples decreased slightly after the defrosting cycles,
349 compared to the values for the samples without exposure to
350 frost tests. Still, no physical deterioration by means of damages
351 or deformations was noticed, indicating that fly-ash-based
352 geopolymers were considerably resistant to frost exposure.
353 Similar conclusions have been reported for fly ash mortars, in
354 comparison to OPC-based specimens.⁷⁹

355 Shu⁸⁰ reported that AAS concrete showed excellent freeze–
356 thaw resistance, thus fitting their application in tunnel lining in
357 extremely cold regions. It was also shown that, using a blend of
358 fly ash and slag in concrete synthesis, the relative dynamic
359 modulus was ~90% after 300 freeze–thaw cycles with a slight
360 mass loss and physical deterioration due to thin surface layers
361 that favorably restrain freeze–thaw damage of concrete. Bilek et
362 al.⁸¹ have reported worse frost resistance in AAMs than in
363 OPC, which was attributed to the presence of a higher amount
364 of free water available for freezing in the structure of alkali-
365 activated concrete. Few results on the effect of FA/BFS on
366 scaling durability of concrete have been reported and discussed
367 by Pigeon et al.;⁸² however, these results were related to OPC-
368 based concrete in which a small amount of FA/BFS (up to
369 20%) has been used as supplementary cementing materials.

From the reported study, no clear conclusions were drawn 370
when OPC was partially replaced by BFS. 371

Based on the given literature review, evaluation of a suitable 372
method for testing in a laboratory environment, replicating in- 373
service conditions, remains to be performed. Determination of 374
parameters related to mix design and sample conditioning is 375
needed in order to define general recommendations for the 376
synthesis of geopolymer binders resistant to freeze–thaw in 377
cold climate zones. 378

Another interesting point that was not deeply investigated 379
through the literature and therefore requires special attention in 380
future works is the relationship between pore structure and 381
frost resistance in AAMs. The nature and particle size of 382
precursor used can strongly affect the pore structure and, 383
consequently, the frost resistance of concrete. 384

2.3. Chloride Resistance. The resistance to chloride attack 385
has been recognized as one of the most concerned aspects of 386
concrete durability. Chloride attack could destroy the 387
passivated layers on the surface of reinforced steel bars, initiate 388
the electrochemical corrosion of steel reinforcement, and 389
consequently reduce the structural capability of concrete 390
elements. Chlorides do not usually harm the concrete matrix 391
as much as its induced corrosion of reinforced steel bars, 392
because the degree of structural change caused by chloride is 393
generally low in portland cement binders and even lower in 394
AAMs.⁸³ Friedel's salt is formed through the conversion of 395
layered calcium sulfoaluminate hydrates into chloroaluminates 396
in OPC mortar after the ponding test of chloride, but the 397
chloride in alkali-activated binders does not involve the 398
formation of crystal phases of new chloroaluminate.⁸⁴ There- 399
fore, the resistance to the transport of chloride ions to the 400
surface of reinforced elements comes to be the first priority in 401
the study of chloride attack in AAMs. 402

The rapid chloride permeability test (RCPT), conforming to 403
ASTM Standard C1202, is widely accepted in practice. The 404
RCPT test, in fact, measures the conductivity of the material, 405
rather than the actual permeability. The effects of conductivity 406
of pore solution, dependency on all the mobile ions rather than 407
the ions of interest, and joule heating on the experimental 408
results make RCPT inadequate, especially when comparing 409
across different types of concretes with different pore solution 410
chemistries. Moreover, the high voltage (typically 60 V) applied 411
for 6 h duration and the associated temperature increase may 412
induce structural damage in the alkali-activated material when 413
using RCPT to assess its chloride permeability.⁸⁵ The non- 414
steady-state migration (NSSM), conforming to NT Build 492, 415
and the ponding test, conforming to ASTM standards, 416
determine the chloride penetration depth by spraying the 417
tested specimens with silver nitrate and offer a better indication 418
of the actual penetration of chlorides into AAMs. Tong et al.⁸⁶ 419
established an approach to evaluate the chloride diffusivity from 420
the test methods of steady-state migration, non-steady-state 421
migration, and electrical conductivity, on the basis of the same 422
test specimens and the same experimental setup; however, the 423
correlations among the test parameters obtained simultaneously 424
are limited to the binder systems of portland cement and silica 425
fume. Yang et al.⁸⁷ quantified the total chloride concentration 426
in the fly-ash–slag-based geopolymer paste through the 427
utilization of X-ray fluorescence (XRF). This newly employed 428
methodology can be used to obtain more-reliable information 429
about the chloride diffusion mechanism in geopolymer systems 430
with a high alkalinity pore solution, when compared to 431
traditional electrical field methods, such as RCPT and NSSM. 432

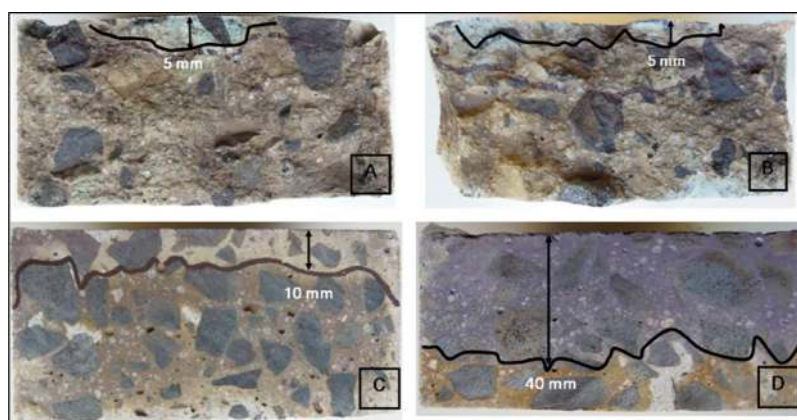


Figure 2. Boundary of chloride penetration in concretes cured for 28 days at the end of the NordTest procedure, as a function of the slag/fly ash ratio: (A) 100 wt % slag, (B) 75 wt % slag/25 wt % fly ash, (C) 50 wt % slag/50 wt % fly ash, and (D) OPC. (Reproduced with permission from ref 84. Copyright 2013, Elsevier BV, Amsterdam.)

To date, there are a limited number of studies on the chloride ingress of AAMs, compared to OPC-based ones, and most of these studies were based on experimental investigation either in the laboratory or in the field. Miranda et al.⁸⁸ reported that the chloride-free activated fly ash mortars were also able to passivate steel reinforcement as quickly and effectively as OPC mortars, but an addition of 2% (by binder weight) of chloride during the mixing operation would multiply the corrosion rate by a factor of ~100. According to Kannapiran et al.,⁸⁹ fly-ash-based reinforced geopolymer concrete beams with heat curing for 24 h revealed no visible traces of corrosion after 180 days of immersion in 5% HCl solution, and the penetration depth of chlorides into concrete was <4 mm, which was much lower than the cover to steel. Kupwade-Patil et al.⁹⁰ studied the durability of steel-reinforced concrete made from alkali-activated fly ash and OPC in a cyclic wet-dry chloride environment over a period of 12 months. The authors found that geopolymer concrete specimens where only microlevel indications of corrosion products were observed via SEM at the matrix/rebar interface exhibited lower average diffusion coefficients, lower chloride contents, and lower porosity, compared with their OPC counterparts where multiple gross corrosion products were observed. Zhu et al.⁹¹ found that (i) the unsaturated alkali-activated fly ash paste and mortar may have higher chloride penetration rate than portland cement paste and mortar, and (ii) only the mortars with a liquid/solid ratio of 0.6 and with 40% slag substitution exhibit a similar chloride penetration rate as the portland cement mortar at $w/c = 0.5$. The RCPT and NSSM tests have been used to evaluate the chloride transport behavior of alkali-silicate-powder-activated slag concrete.⁸⁵ The results showed that the RCPT values of the AAS concrete were generally lower than those of OPC concretes and water-glass-activated slag concretes, while the NSSM coefficients were similar to those of OPC and water-glass-activated slag concretes. According to Ismail et al.,⁸⁴ the chloride migration testing by the NordTest NT Build 492 standard accelerated method and by chloride ponding showed that the diffusion of chloride in AAS-based binders is much lower than that observed in OPC ones (Figure 2), but the volume of permeable voids and sorptivity testing showed that AAS mortar and concrete exhibit higher water absorption than OPC-based samples. The authors attributed this divergence to the specified standard preconditioning (drying) of the samples prior to water absorption testing as drying is likely to induce

desiccation and consequent microcracking of slag-based binding gels.

The chemistry of reaction gels and pore structure significantly controls the transport properties of chloride ions in the AAMs in the chloride-containing environment. Bernal et al.⁶⁰ reviewed the influences of the nature of the binding gel on the chloride permeability in alkali-activated slag/fly ash systems; they concluded that highly durable binders can be designed through the analysis and tailoring of binder gel chemistry. Ismail et al.⁸⁴ mentioned that a denser Al-substituted calcium silicate hydrate (C-A-S-H) gel in AAS concrete contributed to a higher durability under chloride exposure, while the inclusion of fly ash (BFS:FA = 100:0, 75:25, 50:50) promoted the formation of more porous sodium aluminosilicate (N-A-S-H)-type gels, reducing the resistance to chloride ingress.

Yang et al.⁸⁷ reported that the incorporation of slag as a secondary precursor in fly-ash-based geopolymers contributed to the refinement of pore structure and thus restricted the transportation of chloride ions in the paste. Zhu et al.⁹¹ showed that lower porosity and higher tortuosity are both helpful toward decreasing the chloride penetration rate in alkali-activated fly-ash concrete. Ravikumar et al.⁹² investigated the effect of sodium silicate modulus on the chloride penetration of AAS. It has been reported that increasing the $\text{Na}_2\text{O}/\text{slag}$ ratio reduced RCPT and NSSM coefficients of solid sodium silicate-activated slag concretes, and increasing the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of the activator beneficially influenced the transport parameters of liquid sodium silicate-activated slag concretes. The authors mentioned that both the 28-day and 56-day RCPT and NSSM values of AAS concrete decrease as the silica content increases, with a limiting value beyond which the chloride transport parameters are insensitive to the content of silica. They also reported that the powder alkali silicate-activated slag mixtures consistently show better resistance to chloride ion transport than the water-glass-activated mixtures, which can be attributed to a more-refined pore structure indicated by a smaller critical pore size. The same authors reported in one of their recent works⁸⁵ that the critical pore size is more influential than porosity in determining the chloride transport properties of AAS concrete.

Activator dosage in terms of SiO_2 or Na_2O (by binder weight) can significantly affect the resistance to chloride penetration. Chindaprasirt et al.⁹³ reported that the chloride penetration and corrosion of embedded steel in the high-

521 calcium fly-ash-based GPC decreased as the NaOH concen-
522 trations increased, after 3 years of exposure under the marine
523 site, which was attributed to the refinement of the pore
524 structures, as a result of better polycondensation reaction in the
525 relatively high concentration of NaOH. Ma et al.⁹⁴ showed that
526 increasing both the silica and alkali content of the activator
527 results in a lower total porosity and a finer pore system, hence
528 reducing the permeability of alkali-activated fly-ash paste. Law
529 et al.⁹⁵ assessed the durability of AAS concrete with a range of
530 sodium oxide dosages and activator modulus (M_s) values. They
531 found that between $M_s = 1$ and $M_s = 1.25$, the increased
532 reaction of the slag grains is offset by an excess of activator,
533 resulting in fewer, but larger, microcracks. Through the
534 investigation of pore solution and alkali diffusion in fly ash
535 (class F, class C) and slag-based AAM, Lloyd et al.⁹⁶ reported
536 that these systems are prone to alkali leaching, because the
537 alkalis are highly mobile in the pore system, making their
538 retention difficult. The authors suggested the use of a Ca-rich
539 precursor as an effective way for reducing alkali mobility and
540 consequently to keep the pore solution alkalinity at an adequate
541 level, which may avoid steel corrosion and improve the
542 resistance to chloride attack.

543 Thus far, there have been some aforementioned studies on
544 the chloride permeability of AAMs from the point of view of
545 either scientific or technical research, but it is far enough as
546 many challenges are still confronted ahead. The factors
547 affecting the binding capacity of chloride in portland cement-
548 based materials have been studied extensively,⁹⁷ but they are
549 not yet studied comprehensively in AAMs. Many researchers
550 have investigated the chloride permeability of AAMs in
551 comparison with portland cement-based materials, but there
552 is no explicit and uniform criterion for the selection of its
553 counterpart to compare. Many experimental studies have been
554 conducted on the chloride permeability, but the database of
555 chloride migration coefficients is not sufficient for AAMs.
556 Consequently, another challenge is presented, in that modeling
557 chloride transport in AAMs is scarce, because of insufficient
558 information describing chloride penetration with time.⁶⁰ There
559 are some proposed hypotheses in the research of chloride
560 ingress, but they are not yet studied in detail (for example, the
561 sorption of chlorides on the secondary layered double
562 hydroxide phases forming in AAMs⁸⁷). In portland cement
563 and its blended cement concretes, the relationships between
564 chloride penetration and other performance properties have
565 been well-documented, but these relationships are not
566 established in AAMs. All of these challenges provide significant
567 indications for further research to contribute to the study of
568 chloride attack in AAMs.

569 **2.4. Carbonation Resistance.** Carbonation is the chemical
570 reaction taking place between the reaction products of a
571 cementitious matrix and the CO_2 in the atmosphere, promoting
572 the formation of carbonates. In OPC concretes, the pH is
573 mainly controlled by the amount of portlandite ($\text{Ca}(\text{OH})_2$);
574 however, in the case of GPC and AAMs, the pH of the system
575 is mainly controlled by the pore solution. Thus, the carbonation
576 mechanism in these binders occurs in two stages: first,
577 carbonation of the pore solution, leading to a reduction on
578 pH and precipitation of Na-rich carbonates; then, decal-
579 cification of the gel and structure deterioration.^{35,98–101}

580 The process of carbonation is mainly controlled by reactivity
581 and diffusivity of CO_2 . Diffusivity of CO_2 is more related to the
582 interconnectivity of the pore structure and the carbonation
583 exposure conditions while reactivity of CO_2 is related to its

concentration, type of binder, the gel maturity and chemistry of 584
pore solution.¹⁰² It is evident that concentration of CO_2 plays 585
an important role for both reactivity and diffusivity, affecting 586
the carbonation rate during material exposure. 587

Applying more than 1% CO_2 under laboratory conditions 588
during accelerated carbonation significantly underestimates the 589
service life of alkali-activated binders, as reported by Bernal et 590
al.⁹⁸ According to the authors, during natural carbonation, 591
evolution of the binder structure requires a long period of time 592
(years), while accelerated tests are applied on relatively young 593
concretes for a short period of time (weeks). Thus, the 594
influence of gel maturity is essential when analyzing the results 595
of accelerated carbonation exposure. Based on thermodynamic 596
calculations and XRD results, they established a relationship 597
between alkalinity and $\text{CO}_3^{2-}/\text{HCO}_3^-$ ratios in simulated pore 598
solutions with different concentrations of NaOH added in the 599
activator, for natural (0.04% CO_2) and accelerated (4% CO_2) 600
carbonation. The pH reduction in pore solution, because of 601
accelerated carbonation, was 2 orders of magnitude lower, in 602
comparison with natural carbonation exposure. The pH has a 603
tendency to increase as the NaOH concentration increases up 604
to 0.5 mol/kg; after that, the composition of pore solution does 605
not change significantly. It was noted that if the accelerated 606
carbonation is applied to induce steel corrosion of alkali- 607
activated binder, the results will not be representative of in- 608
service performance under natural conditions, because of the 609
rapid decrease in pH in the pore solution and extensive 610
degradation at high CO_2 concentration during testing. 611

The effect of exposure conditions (i.e., concentration of CO_2 , 612
temperature, and relative humidity in accelerated carbonation 613
testing of AAMs) has been investigated by Byfors et al.¹⁰³ and 614
recently by Bernal et al.¹⁰⁴ The lower carbonation rates at 615
higher relative humidity values ($\text{RH} > 80\%$) was attributed¹⁰¹ 616
to the fact that the pores are waterlogged and almost fully 617
saturated with moisture, so the diffusivity of CO_2 is significantly 618
reduced, even when a higher concentration of CO_2 is applied, 619
as stated by Houst et al.¹⁰⁵ Similar conclusions have been 620
reported where testing samples with low water absorption (i.e., 621
initially highly saturated and refined pore networks) at high RH 622
gives a very low carbonation rate in the early stages of the 623
test.¹⁰⁴ On the other hand, at lower relative humidity values 624
($\text{RH} < 50\%$), the diffusivity of CO_2 also decreases, because of 625
unsaturated conditions in the pore structure of concrete, 626
hindering the solvation and hydration of the CO_2 to form 627
carbon acid. The level of relative humidity widely used in 628
accelerated carbonation testing of OPC concrete is $\text{RH} = 50\%$ – 629
70%, providing the best results, which almost reproduced real 630
in-service conditions of concrete carbonation.^{105–109} The 631
highest carbonation rates reported in alkali-activated BFS– 632
metakaolin systems were observed in specimens exposed at RH 633
 $= 65\% \pm 5\%$, where a partially saturated moisture condition 634
produced the highest volume of permeable pores and 635
accelerated the carbonation reaction process.¹⁰⁴ Although in 636
this work, the authors make a clear correlation between relative 637
humidity and carbonation rate, the disagreement between 638
residual compressive strength and relative humidity trends was 639
not well-documented and still unclear. Another interesting 640
point that was raised by the same authors and, consequently, 641
requires further investigation was the limitation of the 642
phenolphthalein method mostly at higher CO_2 concentrations 643
(3% in their study).¹⁰⁴ 644

Deja¹¹⁰ studied the carbonation depths in AAS mortars and 645
concretes, in comparison with OPC-based specimens. Com- 646

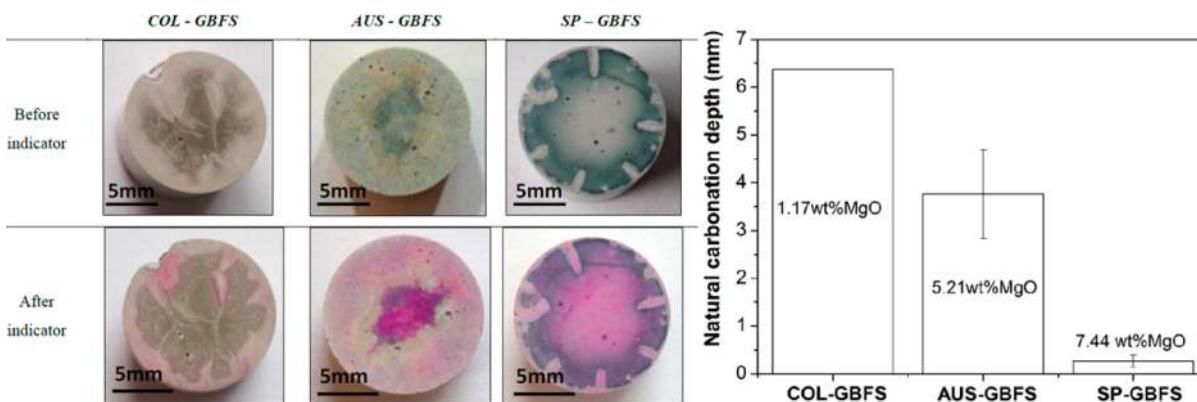


Figure 3. Effect of slag chemistry on carbonation rate in AAS pastes after exposing samples to atmospheric conditions for 16 months. (Reproduced with permission from ref 119. Copyright 2014, Elsevier BV, Amsterdam.)

647 pressive strength was increased at longer exposure times to
 648 carbonation in both binders, because of the precipitation of
 649 carbonates, which resulted in refined pore structure of
 650 specimens. In this study, the relative humidity used (RH =
 651 90%) and CO₂ concentration (100%) values are significantly
 652 higher than those commonly used, which make it difficult to
 653 formulate any relationship or comparison with other results.

654 In a recent study of Bernal et al.,¹¹¹ the AAS concrete
 655 specimens were exposed to the natural carbonation for 7 years.
 656 It was observed that different activation conditions lead to
 657 different carbonation rates. It was also shown that the detected
 658 carbonation depth under accelerated carbonation testing was
 659 relatively higher than that measured under natural conditions.
 660 This was attributed to the thermodynamic differences between
 661 accelerated and natural carbonation conditions, which consid-
 662 erably affects the degradation mechanism under these
 663 conditions. Similar results have been reported on AAS
 664 concrete.⁹⁸

665 The microcracking in partially carbonated AAS concretes was
 666 also observed, which can be associated with the autogenous
 667 shrinkage along the duration of reaction. The same assumption
 668 was made in other works.^{112–114} The authors concluded that
 669 AAS binders can be more susceptible to shrinkage-related
 670 processes than portland-cement-based binders. This was even
 671 emphasized in the early stage of curing.¹¹⁵ In addition, the
 672 extent of shrinkage is considered to be largely affected by the
 673 composition and concentration of the alkaline activator
 674 solution.¹¹⁶

675 The effect of the binder composition and curing conditions
 676 on carbonation rate was extensively studied.^{35,99,111,117–121}
 677 Bernal et al.¹¹⁸ found that the higher amount of paste in AAS
 678 concrete reduced carbonation depth. The authors also reported
 679 that activation conditions—mainly, the concentration of the
 680 activator—greatly influenced the carbonation depth.

681 The influence of slag chemistry on the kinetics of reaction
 682 and the structural evolution of the solid phases forming AAS
 683 binders has been investigated.¹¹⁹ It was found that increasing
 684 the MgO content induced a significant reduction in the
 685 carbonation rate (Figure 3). This phenomenon has been
 686 attributed to the formation of layered double hydroxides with a
 687 hydroxalite-type structure as a secondary reaction product in
 688 systems with high content of MgO (>5 wt %). The advantage
 689 of layered double hydroxides is its ability to absorb CO₂,¹²⁰
 690 thus improving the performance of AAS binders when exposed
 691 to carbonation.

Puertas et al.^{99,100} studied the carbonation of water glass or
 NaOH-activated slag pastes and mortars under saturated CO₂
 conditions. It has been found that, regardless the type of
 activator used, carbonation occurs on and decalcifies the C-S-H
 gel. The mechanical properties of carbonated mortars are
 dependent on the nature of the alkali activator. Using water
 glass, the decalcification of the C-S-H gel leads to a loss of
 cohesion in the matrix, an increase in porosity, and a decline in
 mechanical strength. When NaOH is used, carbonation
 enhanced mortar cohesion, because of the precipitation of
 greater amounts of calcium carbonate in the pores, causing a
 decline in total porosity and average pore size and,
 consequently, an increase in mechanical strength. In the
 water-glass-activated slag systems, no significant effect, either
 on their behavior after carbonation or on the nature of the
 reaction products, has been found after the inclusion of organic
 admixtures. More intense and deeper carbonation was found in
 AAS than in portland cement mortars. Based on their
 experimental results on paste specimens, the author proposed
 two different carbonation mechanisms in OPC and AAS
 systems.¹⁰⁰ In OPC, carbonation occurs in both the portlandite
 and the C-S-H gel, whereas in AAS, carbonation occurs directly
 in the C-S-H gel, probably through the reaction between the
 H₂CO₃ dissolved in the aqueous phase and the Ca²⁺ ions in the
 interlayer zone, between the silicate chains.

Criado et al.¹²¹ studied the effect of curing conditions on the
 carbonation of the reaction products of alkali-activated FA
 systems. It was found that a quick carbonation process could be
 favored if the curing conditions are not suitable. The initial
 carbonation of the system involves the reduction of the pH
 levels; therefore, the ash activation rate and the mechanical
 strength developments are notably slowed. The most
 carbonated phases have been identified in samples that were
 exposed directly in the oven alongside a porcelain capsule
 containing water, regardless of the duration of thermal
 treatment and the type of activator used. The atmospheric
 CO₂ reacts with the sodium present in the system, producing
 sodium bicarbonates instead, which reduces the amount of
 sodium available for the formation of N-A-S-H gel. On the
 other hand, the authors reported that the carbonation does not
 interrupt it, because of the amount of soluble sodium, which
 decreased at longer curing times.

The carbonation of reinforced geopolymer concretes
 produced from three alkali-activated fly ashes with different
 CaO content (1.97, 5.00, and 12.93 wt %, respectively) has
 been recently studied.¹²² Specimens were subjected to

738 accelerated carbonation at 5% CO₂ for a period of 450 days.
739 Changes of concrete structures were determined and electro-
740 chemical measurements were performed over the time of
741 testing to evaluate the effects of carbonation on the corrosion of
742 the steel rebar. Accelerated carbonation induced a considerable
743 reduction in the pH, a reduction in the compressive strength,
744 and a consequent increase in the total porosity in all examined
745 concrete specimens. The reduction in pH is mainly linked to
746 the carbonation of the pore solution according to the fact that
747 sodium carbonates are identified as the main reaction products
748 produced in carbonated specimens. Greater changes in porosity
749 were observed in the case of high-Ca fly-ash-based concretes. It
750 was also concluded that low-Ca class F fly ashes reduced the
751 risk of corrosion in the steel reinforcement to a greater extent
752 than those containing higher levels of Ca, with regard to the
753 chemistry and physical properties of these materials.

754 The carbonation resistance of alkali-activated fly ash, slag, or
755 their blend is mainly influenced by preconditioning of the
756 specimens prior to carbonation testing, carbonation shrinkage
757 induced by decalcification of the binding products, and the
758 chemistry of the pore solution. The standard methodology,
759 which is similar to that which exists for the OPC system, is
760 needed in alkali-activated binders, specifically development of a
761 technique that will imply accelerated carbonation testing.
762 Determination of appropriate exposure conditions, such as
763 the concentration of CO₂, the relative humidity (expressed as a
764 percentage), and the time of exposure needed to replicate a real
765 in-service environment must be postulated. This represents
766 another challenge as the performances of AAMs under
767 accelerated carbonation and natural carbonation have showed
768 some divergences. Shi et al.²⁶ reported a natural carbonation
769 rate of existing aged structures in service, based on AAS
770 concrete, of <1 mm/yr; however, under accelerated carbonation
771 exposures (7% CO₂) for 240 h, a very high carbonation
772 rate (between 13 and 25 mm) was reported.¹²³

773 **2.5. Acid Resistance.** Concrete structures can suffer serious
774 damage when exposed to acidic media such as hydrochloric,
775 acetic, nitric, and sulfuric acids. The most important cause of
776 acid-induced damage to infrastructure elements is biogenic
777 sulfuric acid corrosion, which often occurs in sewer
778 systems.^{124–126} Several studies showed that AAMs, including
779 those derived from high-Ca precursors, exhibit better acid
780 corrosion resistance than portland cement, because of the
781 differences in the nature of their hydration products. Bernal et
782 al.¹²⁷ concluded that AAS exhibits better acid resistance than
783 portland cement, retaining 75% of their original strength after
784 150 days of exposure to acetic acid. Higher stability of AAS
785 binder under acetic acid attack is attributed to lower initial
786 permeability, higher alkalinity of the pore solution, and low
787 CaO/SiO₂ ratio in the AAS system. Decalcification of the AAS
788 binder through formation of calcium acetate leaves a residual
789 aluminosilicate-type gel in the corroded area, which is less
790 soluble and more mechanically sound than the silicate gel
791 formed in portland cement binders, thus contributing to the
792 higher acid resistance of AAS binder.

793 Allahverdi et al. investigated the acid resistance of alkali-
794 activated fly ash and slag mixtures exposed to sulfuric acid
795 solution with different concentrations.^{128,129} The corrosion
796 mechanism of hardened paste at relatively high concentrations
797 of sulfuric acid (pH ~1) consists of two steps. The first step is
798 an ion exchange reaction between the charge-compensating
799 cations of the framework (Na⁺, Ca²⁺) and H⁺ or H₃O⁺ ions
800 from the solution, along with an electrophilic attack by acid

protons on polymeric Si–O–Al bonds. The electrophilic attack
of acid protons results in the ejection of tetrahedral aluminum
from the aluminosilicate framework. In the second step, the
exchanged Ca ions diffusing toward the acid solution react with
counter-diffusing sulfate anions, resulting in the formation and
deposition of gypsum crystals inside a corroding layer, which
provides a protective effect inhibiting the total process of
deterioration. At mild concentrations of sulfuric acid (pH ~2),
the first step of the total corrosion process continues until it
results in the formation of shrinkage cracks. When shrinkage
cracks become wide enough, sulfate anions diffuse into the
cracks, and react with the counter-diffusing Ca ions, resulting in
the formation and deposition of gypsum crystals. At relatively
low concentrations of sulfuric acid (pH ~3) and for limited
periods of exposure time (~90 days), the corrosion mechanism
was described as the leaching of charge-compensating cations
and the ejection of tetrahedral aluminum with no gypsum
deposition, which is identical to that of pH 3 nitric acid.

The durability of geopolymer concrete prepared using
blended ash of pulverized fuel ash and palm oil fuel ash
when exposed to 2% sulfuric acid solution for 18 months have
been investigated by Ariffin et al.¹³⁰ and compared to OPC
performances under the same conditions. From the evaluation
of mass and strength loss, it has been reported that geopolymer
concretes exhibit better acid resistance than OPC, based on
their lower mass and strength loss. While the average mass and
strength loss for geopolymer were 8% and 35%, these
parameters are considerably high for OPC, reaching values of
20% and 68%, respectively. One of the possible reported
explanations to OPC degradation was related to the reaction
between acid and portlandite, which could induce tensile stress,
resulting in cracking and scaling of concrete. However, no
additional information concerning the origin of stress, such as
the nature/type of products formed during the acid–base
reaction and how their formation could affect the micro-
structure integrity, was provided. The decrease in geopolymer
strength was not well documented, and only the breakage of
aluminosilicates bonding was postulated as the main cause of
geopolymer degradation. One important factor that was not
discussed in the reported results and could be responsible for
the decrease on mass and strength is the initial porosity of
geopolymers. This parameter has been deeply analyzed by
Bakharev¹³¹ during a comparative acid resistance study of fly
ash, fly ash+OPC, and OPC specimens. It has been concluded
from this study that the three systems had very similar porosity,
as measured by Brunauer–Emmett–Teller (BET) surface area
analysis (17.5%, 18%, and 16.6%, respectively) but their
performances in durability tests were very different; such
behavior was attributed to the difference in their average pore
diameter, where fly ash geopolymer specimens with a pore
diameter of ~45 Å were the most durable, while OPC
specimens having a pore diameter of ~100 Å were the least
durable in the acidic environment.

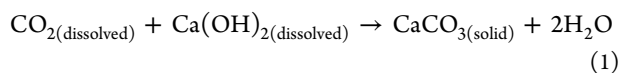
On the other hand, the examination of XRD data before and
after immersion in sulfuric acid solution showed an increase of
zeolite phases (sodalite, natrolite) formed after acid attack,¹³⁰
however, no comment on their effect on the durability of the
geopolymer matrix was reported. Contrarily, Fernandez-
Jimenez et al. reported the destruction of zeolite phases and
dealumination of N-A-S-H gel after immersion in HCl
solution,¹³² however, Bakharev attributed the loss of strength
in fly-ash-based geopolymer (8FAK) exposed to sulfuric acid to
the increased formation of Na–P1 zeolite (gismondine).¹³¹

864 This controversy may be induced either by the type/nature of
865 acid used or even by the anion accompanying the proton/
866 hydronium cation.

867 While the loss in both strength and mass has been widely
868 accepted and used to assess the acid resistance of cement-based
869 materials including AAM, the suitability of these parameters has
870 been subjected to recent debates. Provis et al. reported that the
871 use of compressive strength loss, as a measure of degradation
872 during an accelerated test with a duration of weeks or months,
873 can be complicated by the increase in strength of the
874 undamaged binder regions during the test, which, to some
875 extent, can counteract the strength losses in the degraded
876 binder.⁵ Another drawback reported by the same authors was
877 related to the percentage mass loss measured at a given
878 corrosion depth, which is closely linked to the sample
879 geometry; therefore, a larger sample will lose less strength at
880 the same corrosion depth as a smaller sample, leading to severe
881 difficulties in comparing results between investigations. The
882 corroded depth was proposed to be a better and more suitable
883 parameter than the loss of mass or compressive strength able to
884 be measured with higher accuracy, and reproducibility of the
885 acid resistance of AAM.¹³³

886 Recently, Tahri et al. investigated the resistance to chemical
887 attack (by sulfuric and nitric acid) of fly ash geopolymers for
888 coating portland cement concrete.¹³⁴ It has been found that the
889 fly ash geopolymeric mortar shows a good performance for
890 sulfuric acid concentrations of both 10% and 20%. Even for a
891 sulfuric acid concentration of 30%, this mortar shows good acid
892 resistance for immersion for 14 days. After nitric acid attack, fly-
893 ash-based mortars show a relatively low weight loss (<2%),
894 even after 56 days of immersion, and these materials showed
895 clear vulnerability to acid attack only for a very high
896 concentration (30%), in comparison with other polymeric
897 resins based on epoxy or acrylics. No explicit explanation for
898 the important decrease on fly ash geopolymer mass loss (20%–
899 25% after 14–56 days of exposure to acid attack) was
900 mentioned in their discussion. This decrease in performance
901 could be associated with either the relatively high permeability
902 of fly-ash-based geopolymers, together with their low rate
903 strength development, or the increase in calcium content in the
904 mixture (as they used calcium hydroxide as partial replacement
905 (10%) for fly ash in order to improve mechanical properties).
906 These findings indicated that the role of calcium in alkali-
907 activated material performances remains poorly defined and still
908 need more investigation to draw suitable correlations between
909 calcium content and the engineering and durability properties
910 of the final product.

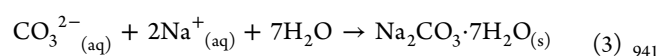
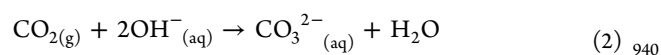
911 **2.6. Efflorescence.** Efflorescence is defined as the
912 formation of a surface deposit that occurs in both natural and
913 artificial environments. It is considered to be a typical surface
914 defect commonly observed on brick, mortar, and concrete
915 facades. This defect is associated with the growth of salt crystals
916 on a surface, originating from the material itself or the
917 surrounding environment and caused by chemical reaction
918 and/or evaporation of the salt solution.^{135,136} In conventional
919 cement-based materials, the most common efflorescence is the
920 formation of calcium carbonate via the following equation:



922 This process was described to occur in six steps: dissolving of
923 $\text{CO}_2(\text{g})$ in H_2O at the air/water interface on the surface of
924 products, conversion of CO_2 to aqueous species, release of

alkalis, dissolution of $\text{Ca}(\text{OH})_2$, diffusion of reactants through
solution, and precipitation of calcium carbonate.¹³⁷ 926

In AAM, mostly those having a porous and open
microstructure (generally with, but not limited to, a low
calcium content such as fly ash), efflorescence is caused by
excess alkali oxide (sodium, potassium, etc.) remaining
unreacted in the material, because of the relative mobility of
the alkali cations within the aluminosilicate framework,
particularly when the material is exposed to cycles of
wetting/drying or moisture transfer. A hydrous alkali carbonate,
 $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, has been identified by XRD analysis as the
main efflorescence product of sodium silicate activated fly
ash.¹³⁸ These results are in agreement with the mechanism of
the efflorescence formation in geopolymers described through
the following equations:¹³⁹ 939



AAM are generally more prone to efflorescence formation,
compared to portland cement. This behavior could be related
to their higher porosity, to the high alkali concentration in the
pore solution, and to the weak binding property of alkali
cations in the aluminosilicate framework.^{133,135,140,141} 946

Efflorescence phenomena have been scarcely investigated,
compared to other AAM issues. In a recently published work, it
has been reported that only ~10 works related to efflorescence
could be found in the literature and only few of them are
directly focused on efflorescence.¹³⁵ One of the most important
reasons that could be related to the lack of research on this
topic is whether efflorescence is considered to be a durability
issue or only a simple aesthetic problem. In some works, it has
been reported that the efflorescence products are whitish and
structurally harmless but aesthetically undesirable.^{5,142} The
same authors consider them to be unsightly, and so it is
desirable to avoid them; however, they are rarely harmful to the
performance of the material. According to other studies, the
efflorescence process was considered only to be unsightly, but
not expansive.^{124,137} Alexander et al. emphasized that, depend-
ing on the environmental conditions, efflorescence can be
observed on the surface of the concrete, or subfluorescence
could occur below the surface, or both.¹²⁴ They also highlighted
that efflorescence is not aesthetically pleasing and can often be
easily eliminated by washing the surface, while subfluorescence
is more likely to generate stresses that will deteriorate the
structure. Recently, Yao et al. investigated the effect of
efflorescence on the compressive strength and shrinkage
property of alkali-activated fly ash and slag blends (BFS:FA =
100:0, 75:25, 50:50, 25:75, 0:100).¹⁴³ Figure 4 shows
efflorescence on the surface of investigated specimens at
different aging regimes. It has been found that efflorescence led
to the strength loss associated with the formation of carbonate
crystals in the binder and the damage of the microstructure.
They also concluded that shrinkage behavior was linked to
efflorescence, in addition to the relative humidity. These latest
results clearly showed that efflorescence is a durability issue
rather than aesthetic problem, since it produced a reduction in
the alkalinity of the binder; the loss of alkalinity may damage
the protective layer around the steel reinforcement, resulting in
its accelerated corrosion and, consequently, the concrete service
life reduction. On the other hand, the efflorescence products
deposited in the binder, mainly alkali carbonates such as 984

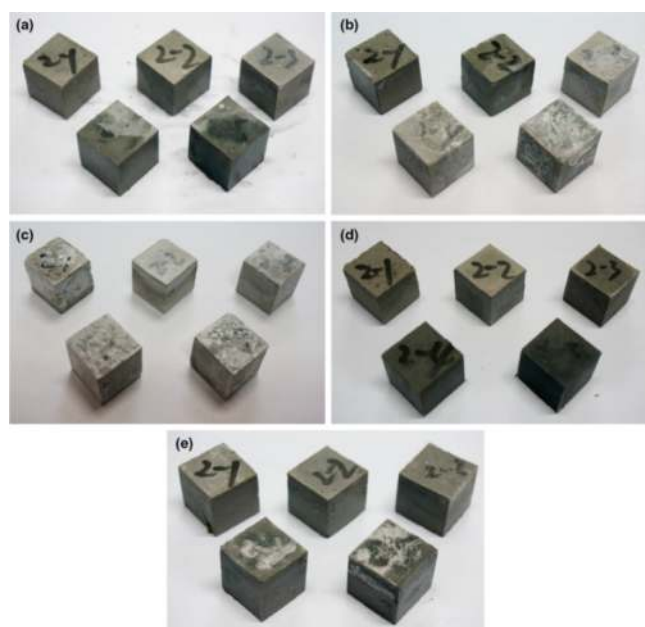


Figure 4. Efflorescence of the alkali-activated fly ash and slag blends with different aging regimes: (a) 7–7bot, (b) 7–28bot, (c) 7–60bot, (d) 7–60con, and (e) 60–60bot. The numbers 2–1 to 2–5 mean the contents of slag, varying from 0% to 100 wt %. Reproduced with permission from ref 143. Copyright 2015, Springer, Berlin, Heidelberg, Germany.)

cured at room temperature than in samples cured at 80 °C under these activation conditions. From the study of hybrid alkaline cements based on fly ash (32%–60%) and portland cement (30%–40%), it has been concluded that no efflorescence was detected in any of the investigated mixtures.¹⁴⁵ The absence of efflorescence was attributed to the low amount of (sodium/potassium), as well as to the fact that some sodium/potassium replaced Ca^{2+} in C-S-H hydration products. Another factor that influences efflorescence is pore volume and permeability. In portland cement, the water participates in the hydration products; therefore, as the hydration progresses, the pore volume decreases over time. While the first reason seems reasonable as the amount of Na/K hydroxide used does not exceed 5%, the second argument is not clear, since no information about the porosity of different investigated mixtures was reported. In addition, this explanation takes into account only the portland cement content: it does not consider the big variation in the amount of fly ash in each mixture (from 32% to 60%) and its effect on total binder permeability.

The use of potassium hydroxide, instead of sodium hydroxide, in the activator was reported to be beneficial in controlling the efflorescence issue,^{5,143,146} because the K^+ cations are strongly bound in the nanostructure of the gel phases in the binder.¹⁴⁰ However, Skvara et al. later reported that both sodium and potassium are weakly bound in the nanostructure of (N,K)-A-S-H gel, and they determined that the alkalis (Na, K) can be almost completely leached from the investigated alkali-activated binder without compromising compressive strength.¹⁴¹ These findings open new debates, first on the role of alkalis in the stability of gel nanostructure and then the efflorescence effect on mechanical properties. A recently published work showed that sodium can partially form Na-O-Al(Si) in the gel structure, in which the Na–O bond is relatively intense, and partially form $\text{Na}(\text{H}_2\text{O})^{n+}$, in which Na is weakly associated with water molecules.¹⁴² The authors were skeptical with the Skvara hypothesis (weakly bonded alkalis in the form of $\text{Na}(\text{H}_2\text{O})^{n+}$) and stated another hypothesis, where alkalis have different states (more than the two discussed above), and each state has its own leaching rate. Concerning the efflorescence effect on compressive strength, most results found in the literature confirmed the negative influence of this process. However, other aspects, such as the relationship between efflorescence and microstructure and how this phenomenon will affect the performances of the final product, are still unclear and need further investigation.

Another aspect of controversy which is still subject to debate and is still unsolved is the differentiation between the process of efflorescence and natural/atmospheric carbonation. While some authors claimed that efflorescence is distinct from the process of natural carbonation as carbonation usually results in binder degradation, pH reduction and the deposition of carbonate reaction products in the bulk of the sample, which may or may not be visible to the naked eye, whereas efflorescence causes the formation of visible surface deposits.^{5,135} However, recent studies showed that efflorescence produced a reduction in alkalis, which could reduce pH and accelerate the corrosion process, and the deposition of alkali salts, which may affect some properties of the AAM.^{142,143} Moreover, the reduced alkali concentration in the matrix due to diffusion toward the surface will affect or suppress the later activation of residual precursors. In addition, the crystallization pressure due to the precipitation of alkali carbonates in the

985 $\text{Na}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$, NaHCO_3 , K_2CO_3 , and KHCO_3 could generate
986 some internal stress leading to volume expansion and/or
987 cracking of the binder.

988 To reduce efflorescence in AAM, different solutions have
989 been proposed. Allahverdi et al.¹³⁵ summarized efflorescence
990 control in three methods: (i) adjustment of chemical
991 formulation of the used alkali activator, (ii) using different
992 curing conditions, and (iii) using different admixtures to
993 enhance microstructure densification of AAM matrix. Najafi
994 Kani suggested that efflorescence can be reduced either by the
995 addition of alumina-rich admixtures such as metakaolin, ground
996 granulated blast-furnace slag, and calcium aluminate cements
997 or by hydrothermal curing.¹⁴⁴ The additional alumina supplied
998 by the high alumina cement admixtures leads to an increased
999 extent of cross-linking in the geopolymer binder, reduces the
1000 mobility of alkalis (which is the key cause of efflorescence in
1001 these materials), and also generates a hardened geopolymer
1002 binder product with markedly improved mechanical properties,
1003 compared to the systems with no admixtures. It has been also
1004 concluded that hydrothermal curing at temperatures of 65 °C
1005 or higher provides a significant effect in efflorescence reduction,
1006 as well as slight strength improvements. Similar results have
1007 been reported by Zhang et al. where a decrease in the
1008 efflorescence rate due to the local reorganization and
1009 crystallization of N-A-S-H gels has been observed after
1010 hydrothermal curing.¹³⁸ In addition, the study of fly ash-
1011 based geopolymers efflorescence behavior was found to be
1012 strongly dependent on the type of alkali activator solution, the
1013 curing temperature, and the slag addition; at the same alkali
1014 content (in terms of Na_2O to solid precursor mass ratio),
1015 soluble silica present in the activator restricts the early age
1016 efflorescence of geopolymers cured at room temperature, but
1017 promotes early age efflorescence at 80 °C. This is mainly
1018 because of the finer pore size distribution developed in samples

1082 pores of the binder may also introduce inner stress and affect
1083 the mechanical properties of AAM.¹⁴² These conclusions make
1084 the distinction between these two processes with the available
1085 knowledge difficult, indicating that additional investigations on
1086 this topic are needed.

1087 The most common durability aspects of AAMs based on fly
1088 ash and/or slag have been reviewed in this work. The main
1089 findings on this topic, as well as the experimental conditions
1090 deduced from some articles referenced in this review, are
1091 summarized in Table S1 in the Supporting Information. It has
1092 been proved that these materials exhibit, when adequately
1093 formulated, similar or even better durability performances than
1094 OPC-based ones. However, a comparison between different
1095 results on AAFA and/or AAS seems to be more difficult,
1096 because of the big divergence in experimental conditions and
1097 testing methods adopted by each group.

1098 The versatility of alkaline activation technology, together
1099 with the availability of a large number of precursors,⁶¹ may
1100 allow the design of several types of cements/concretes with the
1101 required durability performances of the area/region where they
1102 will be used. In the binary slag-fly ash system, these durability
1103 requirements could be achieved by tuning the fly ash/slag ratio
1104 and adjusting other parameters such as the mix design, the
1105 activator (type, dosage), curing conditions, admixtures, etc.

1106 The interest in geopolymers cement/concrete and other
1107 AAMs has increased rapidly in recent years, which has opened
1108 new perspectives for using these materials in many applications
1109 such as construction, infrastructure, nuclear waste immobiliza-
1110 tion, etc. However, the large-scale production and commerci-
1111 alization of AAMs and also their use in bulk construction are
1112 still locked despite the enormous progresses either in
1113 developing new precursors or processing methods and
1114 characterization techniques. The lack of a detailed description
1115 of their durability, together with the lack of appropriate
1116 standards and specifications, are the main issues facing the
1117 entrance and consideration of alkali-activated systems in the
1118 future construction industry.

3. CONCLUDING REMARKS

1119 From this review on the long-term performance of fly ash/slag-
1120 based AAMs during the past decade, the following conclusions
1121 can be drawn:

1122 • Most published results have demonstrated that AAMs have
1123 generally good performances in terms of durability (mostly
1124 their resistance to chemical attacks (acids, sulfates, etc.)).

1125 • The durability of AAMs is mainly controlled by the
1126 chemistry of the pore solution, the microstructure of the
1127 reaction products, and the chemistry of the precursors.

1128 • Most of the testing methods used to investigate long-term
1129 performances of AAMs derived from fly ash, slag, or their
1130 blends are developed the same for checking the durability of
1131 OPC-based systems; however, the difference on chemistry and
1132 structure of these binders, with respect to OPC, could induce
1133 inaccurate results, when adopting these standards.

1134 • Some limitations of common testing methods have also
1135 been identified, such as repeatability and reproducibility of
1136 accelerated carbonation or the determination of the critical
1137 chloride threshold level during chloride penetration test. Many
1138 factors, such as the pH of the concrete pore solution, the
1139 dosage of admixtures, and the detection method, could be
1140 related to these issues.

1141 • The lack of appropriate protocols, specifications, and
1142 standards for a uniform durability testing method to investigate

the durability of fly ash/slag-based AAMs induced some
divergences and even contradictions of some published results,
making any eventual comparison between them more difficult.

• The scientific community and cement industry should
provide the necessary support to technical committees actually
working to develop basic recommendations and standards. This
would help not only AAMs gain acceptance in the marketplace
but also to validate and compare results between different
research groups. RILEM Committees—especially TC 247-
DTA—and the ASTM C01 Committee (Subcommittee
C01.13) have been working the past few years to assess the
suitability of OPC standards for testing the durability of AAMs
and to build the first standards to achieve this goal.

• New advanced characterization techniques either for
precursors or reaction products are needed. Small-angle
neutron and X-ray scattering would reveal the detailed
microstructure that will help to evaluate the microstructural
growth with time as *in situ* experiments can be performed using
these techniques. Raman spectroscopy, confocal microscopy, X-
ray photoelectron spectroscopy, etc. could also provide
important information.

• An accurate description and prediction of thermodynamic
processes involved during gel formation mostly in low-Ca
AAMs requires a developed database to provide all input
parameters needed for this purpose.

• Since durability is directly related to transport phenomena,
a deep understanding of the transport mechanism in geo-
polymer systems and AAMs is still another big challenge.

• Despite the increasing interest in AAMs, which has
provided wide scientific knowledge in this area, some aspects
such as degradation mechanisms under simultaneous deterio-
ration processes still must be investigated deeply for an accurate
evaluation of their durability. This will be very helpful to design
the suitable concrete with the desired performances to specific
conditions under which it will be applied.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.iecr.6b00559.

The most common durability aspects of AAMs based on
fly ash and/or slag have been reviewed in this work. The
main findings on this topic, as well as the experimental
conditions deduced from some articles subjected to this
review, are summarized (Table S1). It has been proved
that these materials exhibit, when adequately formulated,
similar or even better durability performances than OPC-
based ones. However, a comparison between different
results on AAFA and/or AAS seems more difficult,
because of the large divergence in experimental
conditions and testing methods adopted by each group
(PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: k.arbi@tudelft.nl

Notes

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