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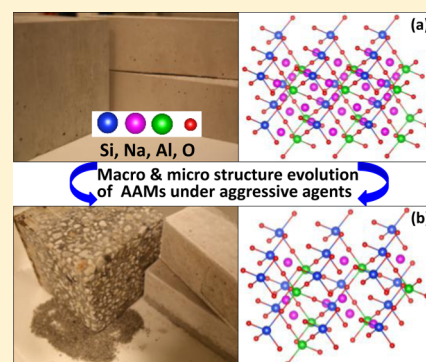
A Review on the Durability of Alkali-Activated Fly Ash/Slag Systems: Advances, Issues, and Perspectives

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S Supporting Information

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



1. INTRODUCTION

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

However, with the current focus on environmental issues, the cement industry causes serious destruction of natural quarries through the extraction of raw materials. It also contributes ~8% of global CO₂ emissions^{3–5} and consumes more than 10% of the total energy used.^{6,7} The total emissions footprint of ~0.8–0.9 t CO₂ per ton of OPC produced are mainly due to the decomposition of limestone (0.53–0.55 t) and the combustion of fossil fuels (0.34–0.39 t) during cement production.^{5,8–10} After the 2009 Copenhagen climate summit, where the international community agreed to keep global average temperature increase below 2 °C, a more significant reduction in CO₂ emissions (20%–50%) was strictly adopted by several countries/continents to guarantee a “normal” human habitability. In this context, the European Union has made a unilateral commitment for 2020 to reduce overall greenhouse gas emissions from its 28 member states by 20%, compared to 1990 levels. In the same way, China, as the world’s largest emitter of CO₂, announced that, by 2020, its carbon dioxide emissions per unit of gross domestic product (GDP) will be

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

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

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

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

2. DURABILITY

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

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

A recent study on the evolution of alkali-activated fly ash/slag (1:1 ratio) pastes exposed to sodium and magnesium sulfate 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

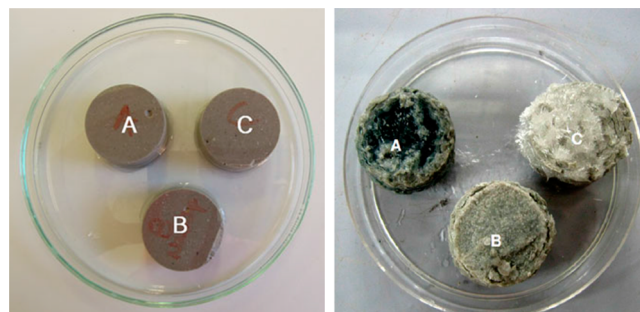


Figure 1. Fly ash/slag specimens aspect after immersion in Na_2SO_4 (left) and MgSO_4 (right) solution for 90 days: (A) w/b 0.40, (B) w/b 0.50, and (C) w/b 0.60. (Reproduced from ref 63. Copyright 2013, Springer, Dordrecht, The Netherlands.)

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 microstructural 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. Moreover, 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
degradation mechanism of aluminosilicate compounds at high
pH is the hydrolysis of the siloxane bonds induced by OH⁻
attack, which later causes desilication of the geopolymer matrix.
Consequently, Si⁴⁺ ions were leached, which was confirmed by
²⁹Si MAS NMR analysis. The decreased Si/Al ratio was one
additional indicator of matrix degradation due to leaching of
Si⁴⁺. The authors attributed the higher observed leaching to the
higher pH of the sulfate solution.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

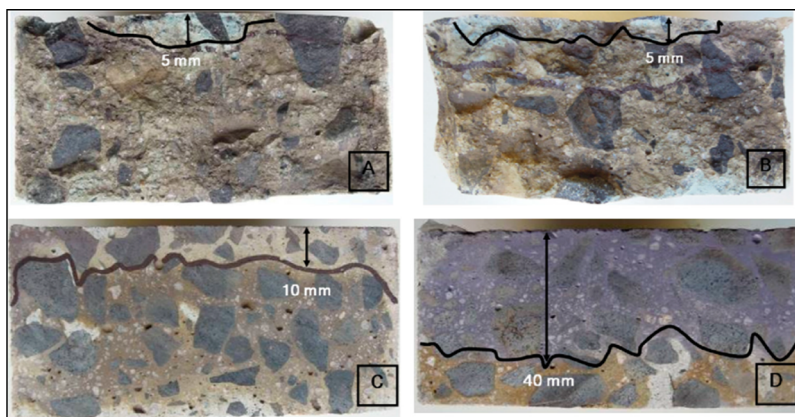


Figure 2. Boundary of chloride penetration in concretes cured for 28 days at the end of the NordTest procedure, as a function of the slag/fly ash ratio: (A) 100 wt % slag, (B) 75 wt % slag/25 wt % fly ash, (C) 50 wt % slag/50 wt % fly ash, and (D) OPC. (Reproduced with permission from ref 84. Copyright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

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

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

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

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

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

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

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

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

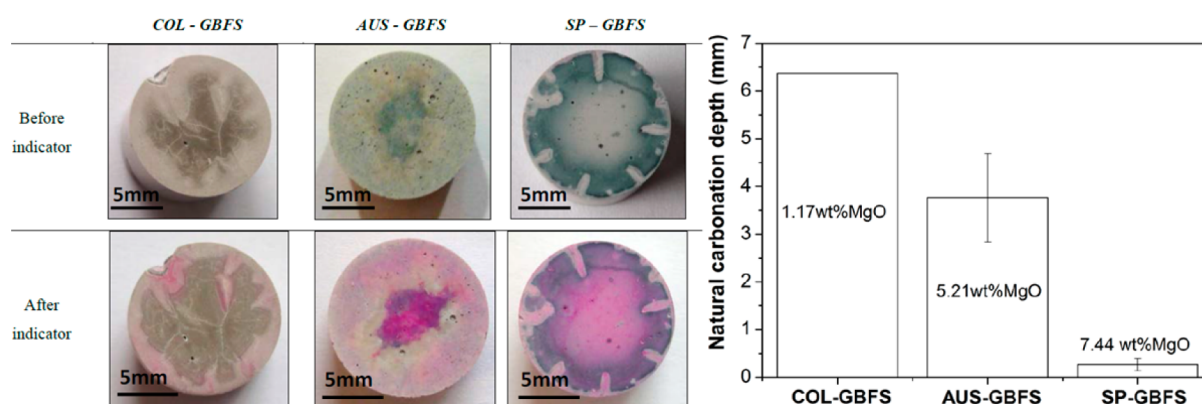


Figure 3. Effect of slag chemistry on carbonation rate in AAS pastes after exposing samples to atmospheric conditions for 16 months. (Reproduced with permission from ref 119. Copyright 2014, Elsevier BV, Amsterdam.)

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

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

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

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

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

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

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

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

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

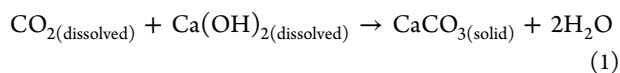
On the other hand, the examination of XRD data before and after immersion in sulfuric acid solution showed an increase of zeolite phases (sodalite, natrolite) formed after acid attack,¹³⁰ however, no comment on their effect on the durability of the geopolymer matrix was reported. Contrarily, Fernandez-Jimenez 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

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

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

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

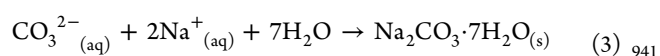
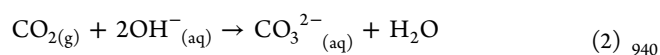
2.6. Efflorescence. Efflorescence is defined as the formation of a surface deposit that occurs in both natural and artificial environments. It is considered to be a typical surface defect commonly observed on brick, mortar, and concrete facades. This defect is associated with the growth of salt crystals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



This process was described to occur in six steps: dissolving of $\text{CO}_2(\text{g})$ in H_2O at the air/water interface on the surface of 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

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



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}

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, depending 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

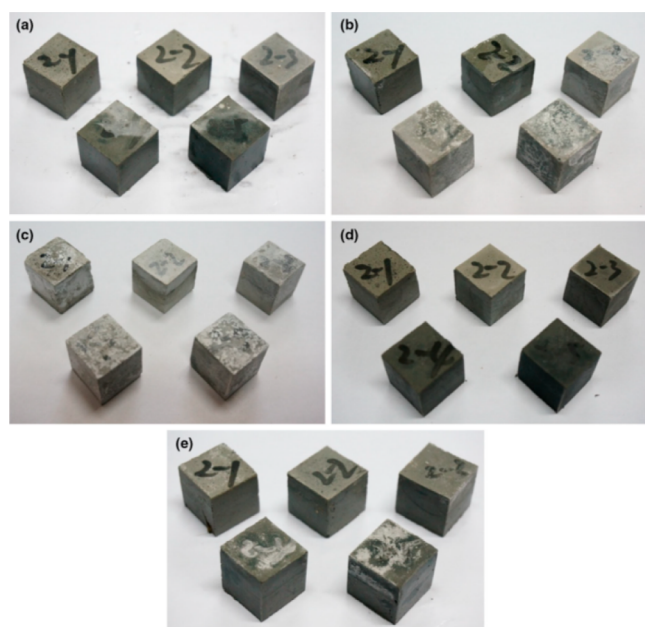


Figure 4. Efflorescence of the alkali-activated fly ash and slag blends with different aging regimes: (a) 7–7bot, (b) 7–28bot, (c) 7–60bot, (d) 7–60con, and (e) 60–60bot. The numbers 2–1 to 2–5 mean the contents of slag, varying from 0% to 100 wt %. Reproduced with permission from ref 143. Copyright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

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

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 referenced in this review, are summarized in Table S1 in the Supporting Information. 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 to be more difficult, because of the big divergence in experimental conditions and testing methods adopted by each group.

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

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

3. CONCLUDING REMARKS

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

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

- The durability of AAMs is mainly controlled by the chemistry of the pore solution, the microstructure of the reaction products, and the chemistry of the precursors.

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

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

- The lack of appropriate protocols, specifications, and 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 geopolymers 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 deterioration 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)

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Notes

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1206 ■ REFERENCES

- 1207 (1) Van Deventer, J. S. J.; Provis, J. L.; Duxson, P. Technical and
1208 commercial progress in the adoption of geopolymers. *Miner. Eng.* **2012**,
1209 *29*, 89.
- 1210 (2) Aitcin, P. C. Cements of yesterday and today; Concrete of
1211 tomorrow. *Cem. Concr. Res.* **2000**, *30*, 1349.
- 1212 (3) Provis, J. L.; Bernal, S. A. Geopolymers and Related Alkali-
1213 Activated Materials. *Annu. Rev. Mater. Res.* **2014**, *44*, 299.
- 1214 (4) Scrivener, K. L.; Kirkpatrick, R. J. Innovation in use and research
1215 on cementitious material. *Cem. Concr. Res.* **2008**, *38*, 128.
- 1216 (5) Provis, J. L.; van Deventer, J. S. J. *Alkali Activated Materials*, State-
1217 of-the-Art Report, RILEM TC 224-AAM; Springer: Dordrecht, the
1218 Netherlands, 2014.
- 1219 (6) Ali, M. B.; Saidur, R.; Hossain, M. S. A review on emission
1220 analysis in cement industries. *Renewable Sustainable Energy Rev.* **2011**,
1221 *15*, 2252.
- 1222 (7) Yang, K. H.; Song, J. K.; Song, K. I. Assessment of CO₂ reduction
1223 of alkali-activated concrete. *J. Cleaner Prod.* **2013**, *39*, 265.
- 1224 (8) Gartner, E. Industrially interesting approaches to low-CO₂
1225 cements. *Cem. Concr. Res.* **2004**, *34*, 1489.
- 1226 (9) Damtoft, J. S.; Lukasik, J.; Herfort, D.; Sorrentino, D.; Gartner, E.
1227 Sustainable development and climate change initiatives. *Cem. Concr.*
1228 *Res.* **2008**, *38*, 115.
- 1229 (10) Pacheco-Torgal, F.; Abdollahnejad, Z.; Camões, A. F.; Jamshidi,
1230 M.; Ding, Y. Durability of alkali-activated binders: A clear advantage
1231 over Portland cement or an unproven issue? *Constr. Build. Mater.*
1232 **2012**, *30*, 400.
- 1233 (11) Liu, L.; Zong, H.; Zhao, E.; Chen, C.; Wang, J. Can China
1234 realize its carbon emission reduction goal in 2020: From the
1235 perspective of thermal power development. *Appl. Energy* **2014**, *124*,
1236 199.
- 1237 (12) Jiao, J.; Qi, Y.; Cao, Q.; Liu, L.; Liang, Q. China's targets for
1238 reducing the intensity of CO₂ emissions by 2020. *Energy Strategy Rev.*
1239 **2013**, *2*, 176.
- 1240 (13) Ukrainczyk, N.; Matusinović, T. Thermal properties of
1241 hydrating calcium aluminate cement pastes. *Cem. Concr. Res.* **2010**,
1242 *40*, 128.
- 1243 (14) Hidalgo Lopez, A.; Garcia Calvo, J. L.; Garcia Olmo, J.; Petit, S.;
1244 Cruz Alonso, M. Microstructural Evolution of Calcium Aluminate
1245 Cements Hydration with Silica Fume and Fly Ash Additions by
1246 Scanning Electron Microscopy, and Mid and Near-Infrared Spectros-
1247 copy. *J. Am. Ceram. Soc.* **2008**, *91*, 1258.
- 1248 (15) Sakai, E.; Sugiyama, T.; Saito, T. M.; Daimon, M. Mechanical
1249 properties and micro-structures of calcium aluminate based ultra-high
1250 strength cement. *Cem. Concr. Res.* **2010**, *40*, 966.
- 1251 (16) Heikal, M.; Morsy, M. S.; Radwan, M. M. Electrical conductivity
1252 and phase composition of calcium aluminate cement containing air-
1253 cooled and water-cooled slag at 20, 40 and 60 °C. *Cem. Concr. Res.*
1254 **2005**, *35*, 1438.
- 1255 (17) Shen, Y.; Qian, J.; Chai, J.; Fan, Y. Calcium sulphoaluminate
1256 cements made with phosphogypsum: Production issues and material
1257 properties. *Cem. Concr. Compos.* **2014**, *48*, 67.
- 1258 (18) Torrén-Martín, D.; Fernández-Carrasco, L.; Martínez-Ramírez,
1259 S. Hydration of calcium aluminates and calcium sulfoaluminate studied
1260 by Raman spectroscopy. *Cem. Concr. Res.* **2013**, *47*, 43.
- 1261 (19) Duan, P.; Chen, W.; Ma, J.; Shui, Z. Influence of layered double
1262 hydroxides on microstructure and carbonation resistance of
1263 sulfoaluminate cement concrete. *Constr. Build. Mater.* **2013**, *48*, 601.
- 1264 (20) García-Maté, M.; Santacruz, I.; De la Torre, Á.G.; León-Reina,
1265 L.; Aranda, M. A. G. Rheological and hydration characterization of
1266 calcium sulfoaluminate cement pastes. *Cem. Concr. Compos.* **2012**, *34*,
1267 684.
- 1268 (21) Juenger, M. C. G.; Winnefeld, F.; Provis, J. L.; Ideker, J. Advances in alternative cementitious binders. *Cem. Concr. Res.* **2011**, *41*, 1232.
- 1270 (22) Grounds, T.; Nowell, D. V.; Wilburn, F. W. Resistance of
1271 supersulfated cement to strong sulfate solutions. *J. Therm. Anal. Calorim.* **2003**, *72*, 181.
- 1273 (23) Liu, S.; Wang, L.; Gao, Y.; Yu, B.; Tang, W. Influence of fineness
1274 on hydration kinetics of supersulfated cement. *Thermochim. Acta* **2015**, *605*, 37.
- 1276 (24) Gruskovnjak, A.; Lothenbach, B.; Winnefeld, F.; Münch, B.; Figi, R.; Ko, S.; Adler, M.; Mäder, U. Quantification of hydration phases in supersulfated cements: Review and new approaches. *Adv. Cem. Res.* **2011**, *23*, 265.
- 1280 (25) Glukhovskiy, V. D. *Soil Silicates* (in Russ.); Gosstroyizdat: Kiev, Ukraine, 1959; p 154.
- 1282 (26) Shi, C.; Krivenko, P. V.; Roy, D. M. *Alkali-Activated Cements and Concretes*; Taylor & Francis: London, 2006.
- 1284 (27) Bignozzi, M. C.; Manzi, S.; Lancellotti, I.; Kamseu, E.; Barbieri, L.; Leonelli, C. Mix-design and characterization of alkali activated materials based on metakaolin and ladle slag. *Appl. Clay Sci.* **2013**, *73*, 78.
- 1288 (28) Zhang, H.; Kodur, V.; Qi, S.; Cao, L.; Wu, B. Development of metakaolin-fly ash based geopolymers for fire resistance applications. *Constr. Build. Mater.* **2014**, *55*, 38.
- 1291 (29) Marjanović, N.; Komljenović, M.; Baščarević, Z.; Nikolić, V.; Petrović, R. Physical-mechanical and microstructural properties of alkali-activated fly ash-blast furnace slag blends. *Ceram. Int.* **2015**, *41*, 1421.
- 1295 (30) Chen, C.; Gong, W.; Lutze, W.; Pegg, I. L. Kinetics of fly ash geopolymers. *J. Mater. Sci.* **2011**, *46*, 3073.
- 1297 (31) Somna, K.; Jaturapitakkul, C.; Kajitvichyanukul, P.; Chindaprasit, P. NaOH activated ground fly ash geopolymer cured at ambient temperature. *Fuel* **2011**, *90*, 2118.
- 1300 (32) Bakharev, T. Geopolymeric materials prepared using Class F fly ash and elevated temperature curing. *Cem. Concr. Res.* **2005**, *35*, 1224.
- 1302 (33) Palomo, A.; Grutzeck, M. W.; Blanco, M. T. Alkali-activated fly ashes: A cement for the future. *Cem. Concr. Res.* **1999**, *29*, 1323.
- 1304 (34) Li, Z.; Liu, S. Influence of slag as additive on compressive strength of fly ash based geopolymer. *J. Mater. Civ. Eng.* **2007**, *19*, 470.
- 1306 (35) Bernal, S. A.; Provis, J. L.; Walkley, B.; San Nicolas, R.; Gehman, J. D.; Brice, D. G.; Kilcullen, A. R.; Duxson, P.; van Deventer, J. S. J. Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation. *Cem. Concr. Res.* **2013**, *53*, 127.
- 1310 (36) Palomo, A.; Alonso, S.; Fernandez-Jimenez, A.; Sobrados, I.; Sanz, J. Alkaline Activation of Fly Ashes: NMR Study of the Reaction Products. *J. Am. Ceram. Soc.* **2004**, *87*, 1141.
- 1313 (37) Ismail, I.; Bernal, S. A.; Provis, J. L.; San Nicolas, R.; Hamdan, S.; van Deventer, J. S. J. Modification of phase evolution in alkali-activated blast furnace slag by the incorporation of fly ash. *Cem. Concr. Compos.* **2014**, *45*, 125.
- 1317 (38) Kumar, S.; Kumar, R.; Mehrotra, S. P. Influence of granulated blast furnace slag on the reaction, structure and properties of fly ash based geopolymer. *J. Mater. Sci.* **2010**, *45*, 607.
- 1320 (39) Bernal, S. A.; Provis, J. L.; Rose, V.; Mejia de Gutierrez, R. Evolution of binder structure in sodium silicate-activated slag-metakaolin blends. *Cem. Concr. Compos.* **2011**, *33*, 46.
- 1323 (40) Arbi, K.; Palomo, A.; Fernández-Jiménez, A. Alkali-activated blends of calcium aluminate cement and slag/diatomite. *Ceram. Int.* **2013**, *39*, 9237.
- 1326 (41) Heikal, M.; Nassar, M. Y.; El-Sayed, G.; Ibrahim, S. M. Physico-chemical, mechanical, microstructure and durability characteristics of alkali activated Egyptian slag. *Constr. Build. Mater.* **2014**, *69*, 60.
- 1329 (42) Davidovits, J. Geopolymers—Inorganic polymeric new materials. *J. Therm. Anal.* **1991**, *37*, 1633.
- 1331 (43) Davidovits, J. *Geopolymer Chemistry and Applications*; Institut Géopolymère; Saint-Quentin, France, 2008.
- 1333 (44) Duxson, P.; Lukey, G. C.; Separovic, F.; van Deventer, J. S. J. The effect of alkali cations on aluminum incorporation in geopolymeric gels. *Ind. Eng. Chem. Res.* **2005**, *44*, 832.

- (45) Duxson, P.; Lukey, G. C.; van Deventer, J. S. J. Characteristics of thermal shrinkage and weight loss in Na-geopolymer derived from metakaolin. *J. Mater. Sci.* **2007**, *42*, 3044–54.
- (46) Provis, J. L.; Lukey, G. C.; van Deventer, J. S. J. Do geopolymers actually contain nanocrystalline zeolites? A reexamination of existing results. *Chem. Mater.* **2005**, *17*, 3075.
- (47) Duxson, P.; Provis, J. L.; Lukey, G. C.; Separovic, F.; van Deventer, J. S. J. ^{29}Si NMR study of structural ordering in aluminosilicate geopolymer gels. *Langmuir* **2005**, *21*, 3028.
- (48) Li, C.; Sun, H.; Li, L. A review: The comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements. *Cem. Concr. Res.* **2010**, *40*, 1341.
- (49) Duxson, P.; Fernández-Jiménez, A.; Provis, J. L.; Lukey, G. C.; Palomo, A.; van Deventer, J. S. J. Geopolymer technology: The current state of the art. *J. Mater. Sci.* **2007**, *42*, 2917.
- (50) Davidovits, J. *Geopolymer Chemistry and Applications*, Second Edition; Institut Géopolymère: Saint-Quentin, France, 2009.
- (51) Komnitsas, K.; Zaharakis, D. Geopolymerisation: A review and prospects for the minerals industry. *Miner. Eng.* **2007**, *20*, 1261.
- (52) Pacheco-Torgal, F.; Castro-Gomes, J.; Jalali, S. Alkali-activated binders: A review. Part 1. Historical background, terminology, reaction mechanisms and hydration products. *Constr. Build. Mater.* **2008**, *22*, 1359–1305.
- (53) Pacheco-Torgal, F.; Castro-Gomes, J.; Jalali, S. Alkali-activated binders: A review. Part 2. About materials and binders manufacture. *Constr. Build. Mater.* **2008**, *22*, 1315.
- (54) Shi, C.; Fernández-Jiménez, A.; Palomo, A. New cements for the 21st century: The pursuit of an alternative to portland cement. *Cem. Concr. Res.* **2011**, *41*, 750.
- (55) Van Deventer, J. S. J.; Provis, J. L.; Duxson, P. Technical and commercial progress in the adoption of geopolymer cement. *Miner. Eng.* **2012**, *29*, 89.
- (56) Rashad, A. M. A comprehensive overview about the influence of different admixtures and additives on the properties of alkali-activated fly ash. *Mater. Eng.* **2014**, *53*, 1005.
- (57) Provis, J. L. Geopolymers and other alkali activated materials: Why, how, and what? *Mater. Struct.* **2014**, *47*, 11.
- (58) Part, W. K.; Ramli, M.; Cheah, C. B. An overview on the influence of various factors on the properties of geopolymer concrete derived from industrial by-products. *Constr. Build. Mater.* **2015**, *77*, 370.
- (59) Palomo, A.; Krivenko, P.; Garcia-Lodeiro, I.; Kavalerova, E.; Maltseva, O.; Fernández-Jiménez, A. Review on alkaline activation: New analytical perspectives. *Mater. Constr.* **2014**, *64*, e022.
- (60) Bernal, S. A.; Provis, J. L. Durability of Alkali-Activated Materials: Progress and Perspectives. *J. Am. Ceram. Soc.* **2014**, *97*, 997.
- (61) Provis, J. L.; Palomo, A.; Shi, C. Advances in understanding alkali-activated materials. *Cem. Concr. Res.* **2015**, *78*, 110.
- (62) Shi, C.; Shi, Z.; Hu, X.; Zhao, R.; Chong, L. A review on alkali-aggregate reactions in alkali-activated mortars/concretes made with alkali-reactive aggregates. *Mater. Struct.* **2015**, *48*, 621.
- (63) Ismail, I.; Bernal, S. A.; Provis, J. L.; Hamdan, S.; van Deventer, J. S. J. Microstructural changes in alkali activated fly ash/slag geopolymers with sulfate exposure. *Mater. Struct.* **2013**, *46*, 361.
- (64) Komljenovic, M.; Bascarevic, Z.; Marjanovic, N.; Nikolic, V. External sulfate attack on alkali-activated slag. *Constr. Build. Mater.* **2013**, *49*, 31.
- (65) Bakharev, T.; Sanjayan, J. G.; Cheng, Y. B. Sulfate attack on alkali-activated slag concrete. *Cem. Concr. Res.* **2002**, *32*, 211.
- (66) Bakharev, T. Durability of geopolymer materials in sodium and magnesium sulfate solutions. *Cem. Concr. Res.* **2005**, *35*, 1233.
- (67) Bhutta, M.; Hussin, M.; Ariffin, M.; Tahir, M. Sulfate resistance of geopolymer concrete prepared from blended waste fuel ash. *J. Mater. Civ. Eng.* **2014**, *26*, 04014080.
- (68) Wallah, S. E.; Rangan, B. V. Low calcium fly ash based geopolymer concrete: Long term properties. Research Report GC2, Faculty of Civil Engineering, Curtin University of Technology, Perth, Australia, 2006.
- (69) Bascarevic, Z.; Komljenovic, M.; Miladinovic, Z.; Nikolic, V.; Marjanovic, N.; Petrovic, R. Impact of sodium sulfate solution on mechanical properties and structure of fly ash based geopolymers. *Mater. Struct.* **2015**, *48*, 683.
- (70) Neville, A. The confused world of sulfate attack on concrete. *Cem. Concr. Res.* **2004**, *34*, 1275.
- (71) Bonakdar, A.; Mobasher, B. Multi-parameter study of external sulfate attack in blended cement materials. *Constr. Build. Mater.* **2010**, *24*, 61.
- (72) Glukhovskiy, V. D. *Alkaline and Alkaline-Alkali-Earth Hydraulic Binders and Concretes* (in Russ.); Vysscha Shkola Publishers: Kiev, USSR, 1979.
- (73) Glukhovskiy, V. D.; Krivenko, P. V.; Rumyna, G. V.; Gerasimchuk, V. L. *The Manufacture of Concretes and Structures from Slag Alkaline Binders*; Budivelnik Publishers: Kiev, USSR, 1988.
- (74) Krivenko, P. V. Alkaline cements. In *Proceedings of the 9th International Congress on the Chemistry of Cement*, New Delhi, India, 1992; Vol. 4-99, p 482.
- (75) Krivenko, P. V. Alkaline cements: Structure, properties, aspects of durability. In *Proceedings of the Second International Conference on Alkaline Cements and Concretes*, Kiev, Ukraine, 1999.
- (76) Fu, Y.; Cai, L.; Yonggen, W. Freeze–thaw cycle test and damage mechanics models of alkali-activated slag concrete. *Constr. Build. Mater.* **2011**, *25*, 3144.
- (77) Cai, L.; Wang, H.; Fu, Y. Freeze–thaw resistance of alkali–slag concrete based on response surface methodology. *Constr. Build. Mater.* **2013**, *49*, 70.
- (78) Škvára, F.; Jilek, T.; Kopecký, L. Geopolymer materials based on fly ash. *Ceram.-Silik.* **2005**, *49*, 195.
- (79) Sun, P.; Wu, H. C. Chemical and freeze–thaw resistance of fly ash-based inorganic mortars. *Fuel* **2013**, *111*, 740.
- (80) Shu, H. A Preliminary Research on Alkali-activated slag concrete as Tunnel Lining in Severe Frigid Regions. *Adv. Mater. Res.* **2013**, *668*, 65.
- (81) Bilek, V.; Szklorzova, H. Freezing and thawing resistance of alkali-activated concretes for the production of building elements. In *Proceedings of 10th CANMET/ACI Conference on Recent Advances in Concrete Technology* (supplementary papers), Seville, Spain, 2009; Malhotra, V. M., Ed.; 2009; p 661.
- (82) Pigeon, M.; Marchand, J.; Pleau, R. Frost resistant concrete. *Constr. Build. Mater.* **1996**, *10*, 339.
- (83) Neville, A. Chloride attack of reinforcement concrete: An overview. *Mater. Constr.* **1995**, *28*, 63.
- (84) Ismail, I.; Bernal, S. A.; Provis, J. L.; San Nicolas, R.; Brice, D. G.; Kilcullen, A. R.; Hamdan, S.; Van Deventer, J. S. J. Influence of fly ash on the water and chloride permeability of alkali-activated slag mortars and concretes. *Constr. Build. Mater.* **2013**, *48*, 1187.
- (85) Ravikumar, D.; Neithalath, N. An Electrical impedance investigation into the chloride ion transport resistance of alkali silicate powder activated slag concretes. *Cem. Concr. Compos.* **2013**, *44*, 58.
- (86) Tong, L.; Gjorv, O. E. Chloride diffusivity based on migration testing. *Cem. Concr. Res.* **2001**, *31*, 973–982.
- (87) Yang, T.; Yao, X.; Zhang, Z. Quantification of chloride diffusion in fly ash-slag-based geopolymers by X-ray fluorescence (XRF). *Constr. Build. Mater.* **2014**, *69*, 109.
- (88) Miranda, J. M.; Fernandez-Jimenez, A.; Gonzalez, J. A.; Palomo, A. Corrosion resistance in activated fly ash mortars. *Cem. Concr. Res.* **2005**, *35*, 1210.
- (89) Kannapiran, K.; Sujatha, T.; Nagan, S. Resistance of reinforced chloride geopolymer concrete beams to acid and chloride migration. *Asian J. Civ. Eng.* **2013**, *14*, 225.
- (90) Kupwade-Patil, K.; Allouche, E. N. Examination of chloride-induced corrosion in reinforced geopolymer concretes. *J. Mater. Civ. Eng.* **2013**, *25*, 1465.
- (91) Zhu, H.; Zhang, Z.; Zhu, Y.; Tian, L. Durability of alkali-activated fly ash concrete: chloride penetration in pastes and mortars. *Constr. Build. Mater.* **2014**, *65*, 51.

- (92) Ravikumar, D.; Neithalath, N. Electrically induced chloride ion transport in alkali activated slag concrete and the influence of microstructure. *Cem. Concr. Res.* **2013**, *47*, 31.
- (93) Chindaprasirt, P.; Chalee, W. Effect of sodium hydroxide concentration on chloride penetration and steel corrosion of fly ash-based geopolymer concrete under marine site. *Constr. Build. Mater.* **2014**, *63*, 303.
- (94) Ma, Y.; Hu, J.; Ye, G. The pore structure and permeability of alkali activated fly ash. *Fuel* **2013**, *104*, 771.
- (95) Law, D. W.; Adam, A. A.; Molyneux, T. K.; Patnaikuni, I. Durability assessment of alkali activated slag (AAS) concrete. *Mater. Struct.* **2012**, *45*, 1425.
- (96) Lloyd, R. R.; Provis, J. L.; Van Deventer, J. S. J. Pore solution composition and alkali diffusion in inorganic polymer cement. *Cem. Concr. Res.* **2010**, *40*, 1386.
- (97) Yuan, Q.; Shi, C.; De Schutter, G.; Audenart, K.; Deng, D. Chloride binding of cement-based materials subjected to external chloride environment—A review. *Constr. Build. Mater.* **2009**, *23*, 1.
- (98) Bernal, S. A.; Provis, J. L.; Brice, D. G.; Kilcullen, A.; Duxson, P.; van Deventer, J. S. J. Accelerated carbonation testing of alkali-activated binders significantly underestimates the real service life: The role of the pore solution. *Cem. Concr. Res.* **2012**, *42*, 1317.
- (99) Puertas, F.; Palacios, M.; Vazquez, T. Carbonation process of alkali-activated slag mortars. *J. Mater. Sci.* **2006**, *41*, 3071.
- (100) Palacios, M.; Puertas, F. Effect of Carbonation on Alkali-Activated Slag Paste. *J. Am. Ceram. Soc.* **2006**, *89*, 3211.
- (101) Bakharev, T.; Sanjayan, J. G.; Cheng, Y. B. Resistance of alkali-activated slag concrete to carbonation. *Cem. Concr. Res.* **2001**, *31*, 1277.
- (102) Fernandez-Bertos, M.; Simons, S. J. R.; Hills, C. D.; Carey, P. J. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂. *J. Hazard. Mater.* **2004**, *B112*, 193.
- (103) Byfors, K.; Klingstedt, G.; Lehtonen, H. P.; Romben, L. Durability of concrete made with alkali-activated slag. In *SP-114: Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete: Proceedings of the Third International Conference*; Malhotra, V. M., Ed.; American Concrete Institute: Farmington Hills, MI, 1989; p 1429.
- (104) Bernal, S. A.; Provis, J. L.; Mejía de Gutierrez, R.; Van Deventer, J. S. J. Accelerated carbonation testing of alkali-activated slag/metakaolin blended concretes: Effect of exposure conditions. *Mater. Struct.* **2015**, *48*, 653.
- (105) Houst, Y. F.; Wittmann, F. H. Influence of porosity and water content on the diffusivity of CO₂ and O₂ through hydrated cement paste. *Cem. Concr. Res.* **1994**, *24*, 1165.
- (106) Houst, Y. F. The role of moisture in the carbonation of cementitious materials. *Int. Z. Bauinstandsetzen* **1996**, *2*, 49.
- (107) Papadakis, V. G.; Vayenas, C. G.; Fardis, M. N. Experimental investigation and mathematical modelling of the concrete carbonation problem. *Chem. Eng. Sci.* **1991**, *46*, 1333.
- (108) Galan, I.; Andrade, C.; Castellote, M. Natural and accelerated CO₂ binding kinetics in cement paste at different relative humidities. *Cem. Concr. Res.* **2013**, *49*, 21.
- (109) Lagerblad, B. Carbon dioxide uptake during concrete life cycle: State of the art. *Swedish Cement and Concrete Research Institute, CBI; Nordic Innovation Centre: Oslo, Norway*, 2006.
- (110) Deja, J. Carbonation aspects of alkali activated slag mortars and concretes. *Silik. Ind.* **2002**, *67*, 37.
- (111) Bernal, S. A.; San Nicolas, R.; Provis, J. L.; Mejía de Gutierrez, R.; Van Deventer, J. S. J. Natural carbonation of aged alkali-activated slag concretes. *Mater. Struct.* **2014**, *47*, 693.
- (112) Collins, F.; Sanjayan, J. G. Cracking tendency of alkali-activated slag concrete subjected to restrained shrinkage. *Cem. Concr. Res.* **2000**, *30*, 791.
- (113) Collins, F.; Sanjayan, J. G. Microcracking and strength development of alkali activated slag concrete. *Cem. Concr. Compos.* **2001**, *23*, 345.
- (114) Palacios, M.; Puertas, F. Effect of shrinkage—reducing admixtures on the properties of alkali-activated slag mortars and pastes. *Cem. Concr. Res.* **2007**, *37*, 691.
- (115) Chi, M. C.; Chang, J. J.; Huang, R. Strength and drying shrinkage of alkali-activated slag paste and mortar. *Adv. Civil Eng.* **2012**, *2012*, 579732.
- (116) Melo Neto, A. A.; Cincotto, M. A.; Repette, W. Drying and autogenous shrinkage of pastes and mortars with activated slag cement. *Cem. Concr. Res.* **2008**, *38*, 565.
- (117) Bernal, S. A.; Mejía de Gutierrez, R.; Rose, V.; Provis, J. L. Effect of silicate modulus and metakaolin incorporation on the carbonation of alkali-activated slags. *Cem. Concr. Res.* **2010**, *40*, 898.
- (118) Bernal, S. A.; Mejía de Gutierrez, R.; Pedraza, A. L.; Provis, J. L.; Rodriguez, E. D.; Delvasto, S. Effect of binder content on the performance of alkali-activated slag concretes. *Cem. Concr. Res.* **2011**, *41*, 1.
- (119) Bernal, S. A.; San Nicolas, R.; Myers, R. J.; Mejía de Gutierrez, R.; Puertas, F.; van Deventer, J. S. J.; Provis, J. L. MgO content of slag controls phase evolution and structural changes induced by accelerated carbonation in alkali-activated binders. *Cem. Concr. Res.* **2014**, *57*, 33.
- (120) León, M.; Díaz, E.; Bennici, S.; Vega, A.; Ordóñez, S.; Auroux, A. Adsorption of CO₂ on hydrotalcite-derived mixed oxides: sorption mechanisms and consequences for adsorption irreversibility. *Ind. Eng. Chem. Res.* **2010**, *49*, 3663.
- (121) Criado, M.; Palomo, A.; Fernandez-Jimenez, A. Alkali activation of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products. *Fuel* **2005**, *84*, 2048.
- (122) Sufian Badar, M.; Kupwade-Patil, K.; Bernal, S. A.; Provis, J. L.; Allouche, E. N. Corrosion of steel bars induced by accelerated carbonation in low and high calcium fly ash geopolymer concretes. *Constr. Build. Mater.* **2014**, *61*, 79.
- (123) Rodríguez, E.; Bernal, S.; Mejía de Gutierrez, R.; Puertas, F. Alternative concrete based on alkali-activated slag. *Mater. Constr.* **2008**, *58*, 53.
- (124) Alexander, M.; Bertron, A.; De Belie, N. *Performance of Cement-Based Materials in Aggressive Aqueous Environments, State-of-the-Art Report*, RILEM TC 211-PAE; RILEM State-of-the-Art Reports, Vol. 10; Springer: New York, 2013.
- (125) Gutiérrez-Padilla, M. G. D.; Bielefeldt, A.; Ovtchinnikov, S.; Hernandez, M.; Silverstein, J. Biogenic sulfuric acid attack on different types of commercially produced concrete sewer pipes. *Cem. Concr. Res.* **2010**, *40*, 293.
- (126) Baščarević, Z. The resistance of alkali-activated cement-based binders to chemical attack. In *Handbook of Alkali-Activated Cements, Mortars and Concretes*; Pacheco-Torgal, F., Labrincha, J. A., Leonelli, C., Palomo, A., Chindaprasirt, P., Eds.; Woodhead Publishing Series in Civil and Structural Engineering, No. 54; Elsevier: Amsterdam, 2015; p 373.
- (127) Bernal, S. A.; Rodríguez, E. D.; Mejía de Gutiérrez, R.; Provis, J. L. Performance of alkali-activated slag mortars exposed to acids. *J. Sustainable Cem.-Based Mater.* **2012**, *1*, 138.
- (128) Allahverdi, A.; Škvára, F. Sulfuric acid attack on hardened paste of geopolymer cements. Part 1. Mechanism of corrosion at relatively high concentrations. *Ceram.—Silik.* **2005**, *49*, 225.
- (129) Allahverdi, A.; Škvára, F. Sulfuric acid attack on hardened paste of geopolymer cements. Part 2. Corrosion mechanism at mild and relatively low concentrations. *Ceram.—Silik.* **2005**, *50*, 1.
- (130) Ariffin, M. A. M.; Bhutta, M. A. R.; Hussin, M. W.; Mohd Tahir, M.; Aziah, N. Sulfuric acid resistance of blended ash geopolymer concrete. *Constr. Build. Mater.* **2013**, *43*, 80.
- (131) Bakharev, T. Resistance of geopolymer materials to acid attack. *Cem. Concr. Res.* **2005**, *35*, 658.
- (132) Fernández-Jiménez, A.; García-Lodeiro, I.; Palomo, A. Durability of alkali-activated fly ash cementitious materials. *J. Mater. Sci.* **2007**, *42*, 3055.
- (133) Lloyd, R. R.; Provis, J. L.; Van Deventer, J. S. J. Acid resistance of inorganic polymer binders. 1. Corrosion rate. *Mater. Struct.* **2012**, *45*, 1.
- (134) Tahri, W.; Abdollahnejad, Z.; Mendes, J.; Pacheco-Torgal, F.; Barroso de Aguiar, J. Performance of a Fly Ash Geopolymeric mortar for coating of ordinary portland cement concrete exposed to harsh chemical environments. *Adv. Mater. Res.* **2015**, *1129*, 573.

- (135) Allahverdi, A.; Najafi-Kani, E.; Hossain, K. M. A.; Lachemi, M. Methods to control efflorescence in alkali-activated cement-based materials. In *Handbook of Alkali-Activated Cements, Mortars and Concretes*; Pacheco-Torgal, F., Labrincha, J. A., Leonelli, C., Palomo, A., Chindaprasirt, P., Eds.; Woodhead Publishing Series in Civil and Structural Engineering, No. 54; Elsevier: Amsterdam, 2015; p 463.
- (136) Chwast, J.; Todorovic, J.; Janssen, H.; Elsen, J. Gypsum efflorescence on clay brick masonry: Field survey and literature study. *Constr. Build. Mater.* **2015**, *85*, 57.
- (137) Dow, C.; Glasser, F. P. Calcium carbonate efflorescence on Portland cement and building materials. *Cem. Concr. Res.* **2003**, *33*, 147.
- (138) Zhang, Z.; Provis, J. L.; Reid, A.; Wang, H. Fly ash-based geopolymers: The relationship between composition, pore structure and efflorescence. *Cem. Concr. Res.* **2014**, *64*, 30.
- (139) Xie, T.; Ozbakkaloglu, T. Behavior of low-calcium fly and bottom ash-based geopolymer concrete cured at ambient temperature. *Ceram. Int.* **2015**, *41*, 5945.
- (140) Škvára, F.; Kopecký, L.; Myšková, L.; Šmilauer, V.; Alberovská, L.; Vinšová, L. Aluminosilicate polymers—Influence of elevated temperatures, efflorescence. *Ceram.—Silik.* **2009**, *53*, 276.
- (141) Škvára, F.; Šmilauer, V.; Hlaváček, P.; Kopecký, L.; Cílová, Z. A weak alkali bond in (N, K)—A—S—H gels: Evidence from leaching and modeling. *Ceram.—Silik.* **2012**, *56*, 374.
- (142) Zhang, Z.; Provis, J. L.; Wang, H. Critical thinking on efflorescence in alkali activated cement (AAC). In *Proceedings of the Second International Conference on Performance-Based and Lifecycle Structural Engineering (PLSE 2015)*, Brisbane, Australia, 2015; Fernando, D., Teng, J.-G., Torero, J. L., Eds.; Paper ID 217, p 147.
- (143) Yao, X.; Yang, T.; Zhang, Z. Compressive strength development and shrinkage of alkaliactivated fly ash–slag blends associated with efflorescence. *Mater. Struct.* **2015**, DOI: [10.1617/s11527-015-0694-3](https://doi.org/10.1617/s11527-015-0694-3).
- (144) Najafi Kani, E.; Allahverdi, A.; Provis, J. L. Efflorescence control in geopolymer binders based on natural pozzolan. *Cem. Concr. Compos.* **2012**, *34*, 25.
- (145) Abdollahnejad, Z.; Hlavacek, P.; Miraldo, S.; Pacheco-Torgal, F.; Barroso de Aguiar, J. L. Compressive Strength, Microstructure and Hydration Products of Hybrid Alkaline. *Mater. Res.* **2014**, *17*, 829.
- (146) Szklorzová, H.; Bílek, V. Influence of alkali ions in the activator on the performance of alkali-activated mortars. In *The 3rd International Symposium on Non-traditional Cement and Concrete* Bilek, V., Kersner, Z., Eds.; Brno, Czech Republic, 2008; p 777.