



Durability of slag-based alkali-activated materials: A critical review

H. S. Gökçe^{1,2}

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Abstract

As the world becomes increasingly aware of the devastating effects of climate change, the need for sustainable building materials that are both durable and environmentally friendly increases. Geopolymer and alkali-activated materials formed by a chemical reaction between an alkaline activator solution and an aluminosilicate source have gained popularity in recent years. The alkaline activator solution dissolves the aluminosilicate source, which then undergoes a polycondensation reaction to form a three-dimensional geopolymeric gel network. The development of this network ensures the strength and durability of the material. Today, this phenomenon of durability has been studied in detail to enable the development of superior construction materials, taking into account degradation mechanisms such as carbonation, leaching, shrinkage, fire, freezing and thawing, and exposure to aggressive environments (chlorides, acids, and sulphates). Although there are many unsolved problems in their engineering applications, slag-based alkali-activated materials appear to be more advantageous and are promising as alternative materials to ordinary Portland cement. First of all, it should not be ignored that the cure sensitivity is high in these systems due to compressive strength losses of up to 69%. Loss of strength of alkali-activated materials is considered an important indicator of degradation. In binary precursors, the presence of fly ash in slag can result in an improvement of over 10% in compressive strength of the binary-based alkali-activated materials after undergoing carbonation. The binary systems can provide superior resistance to many degradation mechanisms, especially exposure to high-temperature. The partial presence of class F fly ash in the slag-based precursor can overcome the poor ability of alkali-activated materials to withstand high temperatures. Due to the desired pore structure, alkali-activated materials may not be damaged even after 300 freeze–thaw cycles. Their superior permeability compared to cementitious counterparts can extend service life against chloride corrosion by more than 20 times. While traditional (ordinary Portland cement-based) concrete remains the most widely used material in construction, geopolymer concrete’s superior performance makes it an increasingly emerging option for sustainable and long-lasting infrastructure.

Keywords Alkali-activated materials · Geopolymers · Ground blast furnace slag · Durability

Introduction

Geopolymer and alkali-activated material technology is still in its early stages. Therefore, a lot of research is being carried out to improve the quality, economy and environmental cost-effectiveness of such materials [1–4]. Although geopolymers and alkali-activated materials are defined separately by Davidovits [5] due to their different chemistries

that play a critical role in their durability, van Deventer et al. [6] define geopolymers as a special type of alkali-activated materials. Based on the data from Scopus (see Fig. 1) [7], these binders developed by CaO-dominated precursors such as slag are often referred to as alkali-activated materials rather than geopolymers [8]. In this critical review, both of these terms have been used to describe these materials as presented in the address sources.

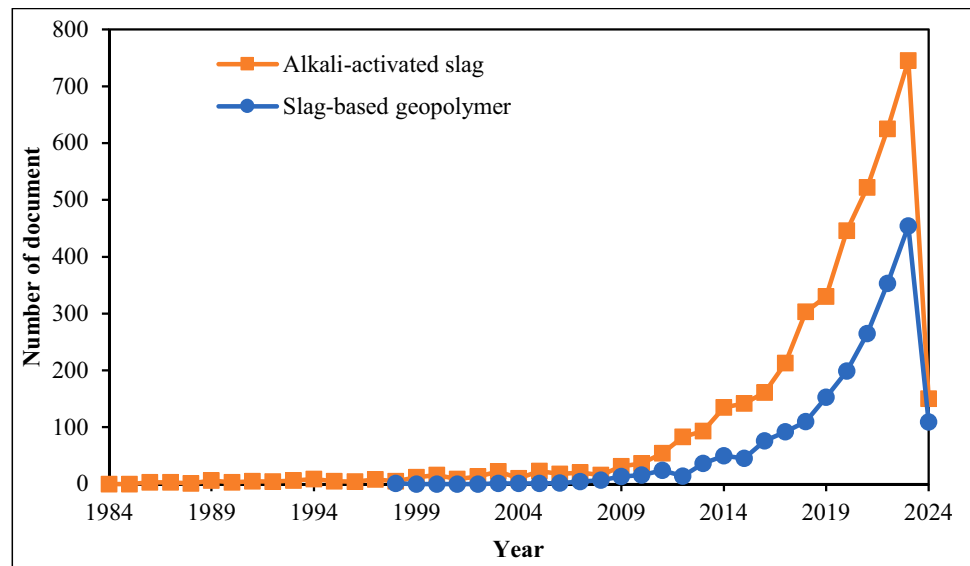
Researchers are exploring new methods to produce geopolymer materials [9, 10] as well as new areas of application to meet the current construction needs [11–13]. One of the research areas focuses mainly on the development of activators for these materials that can improve their performance and reduce costs. Another area of research is focused on developing feasible applications for geopolymer materials

✉ H. S. Gökçe
suleyman.gokce@idu.edu.tr

¹ Department of Civil Engineering, Izmir Democracy University, Izmir, Türkiye

² Department of Civil Engineering, Bayburt University, Bayburt, Türkiye

Fig. 1 Number of documents from 1984 to 2024, which include “alkali-activated slag” and “slag-based geopolymer” in their title, abstract, and keywords



such as 3D printing and prefabricated building components. Overall, the future looks bright for alkali-activated material technology as it continues to gain popularity as a sustainable and long-lasting (durable) construction material [14]. The issue of durability examined in contemporary materials dates back to ancient times. “De Architectura” a series of books by the architecture Marcus Vitruvius Pollio (probably dating back to between 30–20 BC), is the first printed evidence of primitive approaches to the durability of building materials [15]. Today, understanding the causes of carbonation, leaching, efflorescence, shrinkage, resistance to fire, freeze–thaw, and aggressive environments, and the solutions to deterioration mechanisms has become essential in order to ensure the durability, strength, and safety of the material. By optimizing the mix design, using appropriate curing methods, and incorporating specific additives, engineers and builders can overcome the emerging challenges and improve the specified durability performances of the material [16–24].

The geopolymer binders can be synthesized by a number of precursor sources in alkaline or acidic environments [25–27]. Slag (ground granulated blast furnace slag), a by-product of the ever-growing steelmaking industry, is becoming the most promising precursor in terms of cost, environmental and sustainability concerns in the near future when compared to residues or products from other industries such as fly ash, metakaolin and red mud. The existence of an exothermal reaction mechanism between the activator and CaO in the slag allows the geopolymerization process without thermal curing [28, 29]. Accordingly, the content of this paper is mostly addressed with data obtained from the test results of slag-based alkali-activated materials cured at ambient temperatures. This content has been supported by the partial use of other aluminosilicate sources, which have a much larger crystalline phase, reactive alumina, and lower

CaO content, requiring a special curing regime [19, 30–32]. In contrast to the advantage of alkali-activated slag to easily gain strength at ambient temperatures, the stability of the resulting geopolymerization gels such as C-(N)-A-S-H and weakly linked Si networks ($\leq Q_2$) for leaching out in contact with water is highly questionable [33]. Many studies have been conducted to understand its degradation mechanism, especially on carbonation [34–37], leaching [38–41], shrinkage [42–45], fire [46–49], freezing and thawing [50–53], and exposure to aggressive environments (chlorides, acids, and sulphates) [54–61].

The durability aspects of alkali-activated slag pose challenges for researchers working in cement and concrete technology due to the complexity of their design compared to the well-established chemistry of ordinary Portland cement. Although today’s research may seem like a small step, all scientific initiatives are necessary to contribute to overcoming these current challenges. The author believes that this critical review on the durability of geopolymer and alkali-activated material will encourage researchers to produce these sustainable materials from blast furnace slag, a by-product of vital industry (iron and steel), rather than by-products of other industries (e.g., coal-fired thermal power plants), which is under discussion due to global warming.

Objectives, methodology and data analysis

The term “durability” has recently gained popularity in many fields of science, especially in engineering, as seen in Fig. 2 [62]. Only 3.4% of these documents (in engineering field) are review documents. The number of review studies addressing research articles on durability has become critical to responding to the world’s sustainability goals.

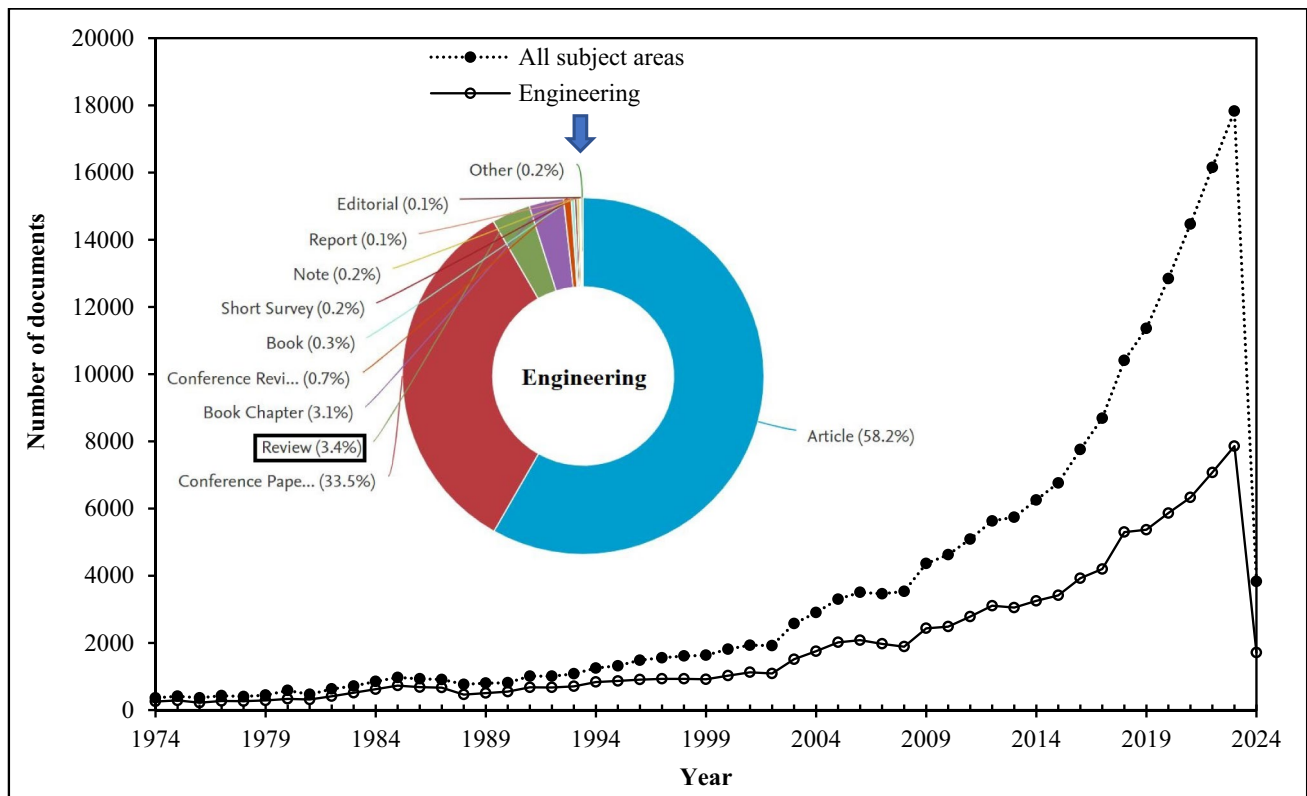


Fig. 2 Data analysis of the number of scientific documents on “durability” from 1974 to 2024

This critical review aims to investigate the degradation of alkali-activated slag/slag-based geopolymer when exposed to the deterioration mechanisms commonly encountered in the construction industry.

Considering the large number of relevant publications, a specific methodology was followed to consider the most suitable documents to be included in the literature search to achieve the above-mentioned aims of the critical review. Accordingly, a systematic approach was adopted: (I) identifying the most relevant keywords; (II) listing relevant publications obtained from Google Scholar, Web of Science, and Scopus databases; (III) ignoring documents that are out of scope or unnecessary after a preliminary analysis focusing on the title, abstract and concluding remarks; (IV) second screening to focus more on the most relevant documents, taking into account more details of the available documents; (V) deciding on the final list of documents and outline of the paper; (VI) writing the first draft; (VII) determining weak parts of the draft; (VIII) researching additional documents with new keywords to strengthen weak sections; (IX) adequately addressing durability aspects of alkali-activated slag/slag-based geopolymer in the text; (X) critically discuss and develop results, and identify the need for future perspective; (XI) concluding the final text of this study. Accordingly, a total of 188 documents obtained from journals, conferences,

books, and the Internet were examined and discussed in this critical review. A significant part of these documents was taken from reputable journals. In order to better contribute to the collective knowledge in the field, 66% of the references are current sources published in the last five years (2018–2023). Table 1 lists the category, source, and number of these documents.

Carbonation, leaching, and efflorescence

As a quantitative indicator of durability, the link between strength loss and degradation mechanism is mainly investigated in studies for geopolymers [63–65]. In addition to environmental variables, some compositional characteristics, including microcracks, porosity (determining the diffusivity of CO_2 into the matrix), and water availability in the pores, are the well-known parameters affecting the carbonation rate of composites [66]. The presence of unbonded and solved alkalis (Na and K) and calcium ions is the main reason for these types of degradation in geopolymers when exposed to certain environmental conditions. A reduction in strength results from the carbonation of free alkalis (Na, and K) not playing a role in geopolymerization reactions [67]. In addition, a lower pH below 11 may induce the risk of corrosion of the reinforcing

Table 1 Category, source, and numerical analysis of documents

Category	Source	Number	%	
Journal	Construction and Building Materials	50	26.6	93.6
	Cement and Concrete Research	16	8.5	
	Cement and Concrete Composites	8	4.3	
	Journal of Building Engineering	8	4.3	
	Journal of Cleaner Production	8	4.3	
	Case Studies in Construction Materials	5	2.7	
	Composites Part B: Engineering	5	2.7	
	Advances in Cement Research	3	1.6	
	Ceramics International	3	1.6	
	Journal of Materials in Civil Engineering	3	1.6	
	Materials (Basel)	3	1.6	
	Arabian Journal for Science and Engineering	2	1.1	
	Engineering	2	1.1	
	Materialia	2	1.1	
	Materials and Structures	2	1.1	
	Materials Letters	2	1.1	
	Materials Today: Proceedings	2	1.1	
	Journal of Hazardous Materials	2	1.1	
	Journal of Materials Science	2	1.1	
	Journal of Sustainable Cement-Based Materials	2	1.1	
	Polymers (Basel)	2	1.1	
	Silicon	2	1.1	
	Structural Concrete	2	1.1	
	ACS Omega	1	0.5	
	Advances in Civil Engineering	1	0.5	
	Ain Shams Engineering Journal	1	0.5	
	Annual Review of Materials Research	1	0.5	
	Arabian Journal of Chemistry	1	0.5	
	ARPJ Journal of Engineering and Applied Sciences	1	0.5	
	Ceramics-Silikáty	1	0.5	
	Coatings	1	0.5	
	Corrosion Science	1	0.5	
	Crystals	1	0.5	
	Developments in the Built Environment	1	0.5	
El-Cezeri Journal of Science and Engineering	1	0.5		
European Journal of Environmental and Civil Engineering	1	0.5		
Fuel	1	0.5		
Geopolymer Institute Library	1	0.5		
International Journal of Civil Engineering	1	0.5		

Table 1 (continued)

Category	Source	Number	%	
	International Journal of Damage Mechanics	1	0.5	
	International Journal of Minerals, Metallurgy, and Materials	1	0.5	
	International Journal of Sustainable Engineering	1	0.5	
	Iranian Journal of Science and Technology, Transactions of Civil Engineering	1	0.5	
	Journal of Building Physics	1	0.5	
	Journal of Ceramic Science and Technology	1	0.5	
	Journal of Environmental Management	1	0.5	
	Journal of Material Cycles and Waste Management	1	0.5	
	Journal of Materials and Environmental Sciences	1	0.5	
	Journal of Materials Research and Technology	1	0.5	
	Journal of Non-Crystalline Solids	1	0.5	
	Journal of Petroleum Science and Engineering	1	0.5	
	Journal of Wuhan University of Technology-Mater. Sci. Ed	1	0.5	
	Magazine of Concrete Research	1	0.5	
	Materials and Design	1	0.5	
	Microporous and Mesoporous Materials	1	0.5	
	Minerals	1	0.5	
	Reviews on Advanced Materials Science	1	0.5	
	Science of The Total Environment	1	0.5	
	Scientia Iranica	1	0.5	
	Structures	1	0.5	
	Transactions of Nonferrous Metals Society of China	1	0.5	
	Waste and Biomass Valorization	1	0.5	
	Waste Management	1	0.5	
Conference	CONCES 2004	3	1.6	3.2
	IOP Conference Series	1	0.5	
	SPE/IADC International Drilling Conference and Exhibition	1	0.5	
	The Saudi International Building and Constructions Technology Conference	1	0.5	
Book	CRC Press	1	0.5	2.1
	Elsevier	1	0.5	
	Harvard University Press	1	0.5	
	RILEM Bookseries	1	0.5	
Internet	Scopus	2	1.1	1.1
Total		188	100.0	100.0

steel [68]. Due to the role of CaO in C-(N)-A-S-H gels and pH, Ca-rich slag content contributes to the carbonation resistance of geopolymers, and even to some extent improvement in strength can be achieved at various carbonation exposures [69]. An increment in the initial pH (from 10.8 to 12.2) of geopolymers, including slag in terms of fly ash, can be documented to be another reason for the lower carbonation level and its benefit in mechanical results, as given in Fig. 3.

The leaching potential of geopolymer composites has not been reported enough, while numerous studies evaluate the leaching potential of ordinary Portland cement composites [70]. Besides, the leaching of geopolymers requires more attention than cement counterparts due to additional concerns. Not only does its durability suffer from the dissolution of aluminosilicate gel and free alkali ions, but geopolymer can create a further threat for the

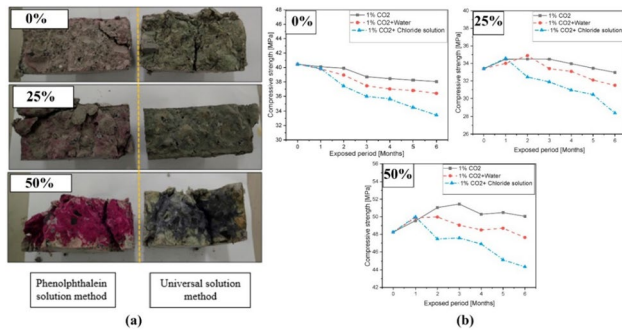


Fig. 3 Carbonation statement (a) and strength variations (b) of geopolymer samples at various amounts of GGBS [69]

environment as it contains high-volume industrial by-products with concentrated toxic heavy metal contents [71, 72]. Upcycling these industrial wastes into composites can limit the leakage potential of toxic metals into the ground by capturing them in geopolymeric products. In fact, Sun and Vollpracht [73] stated that As, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sb, Se, Tl, and Zn are in similar leaching amounts with the cement-based counterparts except V and Mo. These leachable toxic contents of geopolymers are directly proportional to the leachable contents in precursors [71]. On the other hand, when specimens are exposed to water, leaching of unreacted sodium silicate can cause up to a 25% strength loss [74]. Under open curing conditions, interruption of geopolymeric reactions by water evaporation may result in a higher strength loss reaching 69% due to the solid body's increased porosity (around 50%) [75].

While a high concentration of alkalis is required for favorable strength development of geopolymers, it increases the solubility and absorption rate of CO₂ and accelerates efflorescence [76]. The visible deposits of efflorescence on the surface can or cannot result in the degradation of geopolymeric structures depending on the original strength, porosity, and crystallization pressure [77, 78]. Silica modulus (Ms, SiO₂/Na₂O ratio) is one of the most pronounced characteristics of geopolymers' strength, porosity, and leachable alkalis [79–81]. Thus, original strength and its loss can be significantly affected by its variation, as seen in Fig. 4. To be a deleterious and internal part of the efflorescence mechanism, subflorescence in pores below 360 nm creates excessive pressure compared to the tensile strength capability of geopolymer products during the evaporation of water [82, 83]. According to Zhang et al. [84], even if the relationship between subflorescence and tensile strength has not been investigated by experiments, its impact cannot be ignored for understanding the fracture mechanism of geopolymers.

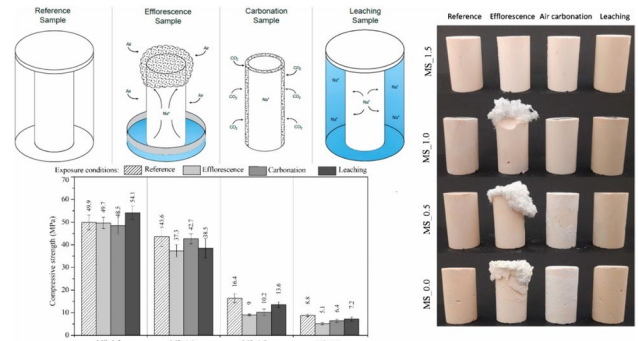


Fig. 4 Mechanical deterioration of geopolymer samples with various silica modulus (Ms) ranging from 0 to 1.5 [85]

Shrinkage

One of the biggest challenges that engineers and builders face is the issue of shrinkage when working with geopolymer and alkali-activated materials. Shrinkage is the reduction in the size or volume of a material, which can lead to cracking, reduced strength, and ultimately compromise the structural integrity of a building [86, 87]. Four types of shrinkage can occur in geopolymer and alkali-activated materials: chemical, autogenous, drying, and carbonation shrinkage. The chemical shrinkage, which occurs when the volume of the reaction products is less than its ingredients, and the autogenous shrinkage, which results from the increase in capillary pressure in the matrix, are defined in the same way up to the initial setting [88]. Autogenous shrinkage occurs when the material undergoes self-desiccation during the setting and hardening process. The water consumed during the chemical reaction is not replaced, which can result in shrinkage. This shrinkage typically occurs in the early stages of the hardening process. Drying shrinkage occurs when the material loses moisture due to evaporation. This can occur during the curing process, or after the material has been placed in its final position. Drying shrinkage can be particularly problematic in hot and dry climates, where evaporation rates are high. Carbonation shrinkage occurs when carbon dioxide in the atmosphere reacts with the alkaline activator solution in the material. This can cause the material to expand initially, but over time, the reaction can lead to shrinkage. Carbonation shrinkage is typically a long-term issue and can take years to manifest [89].

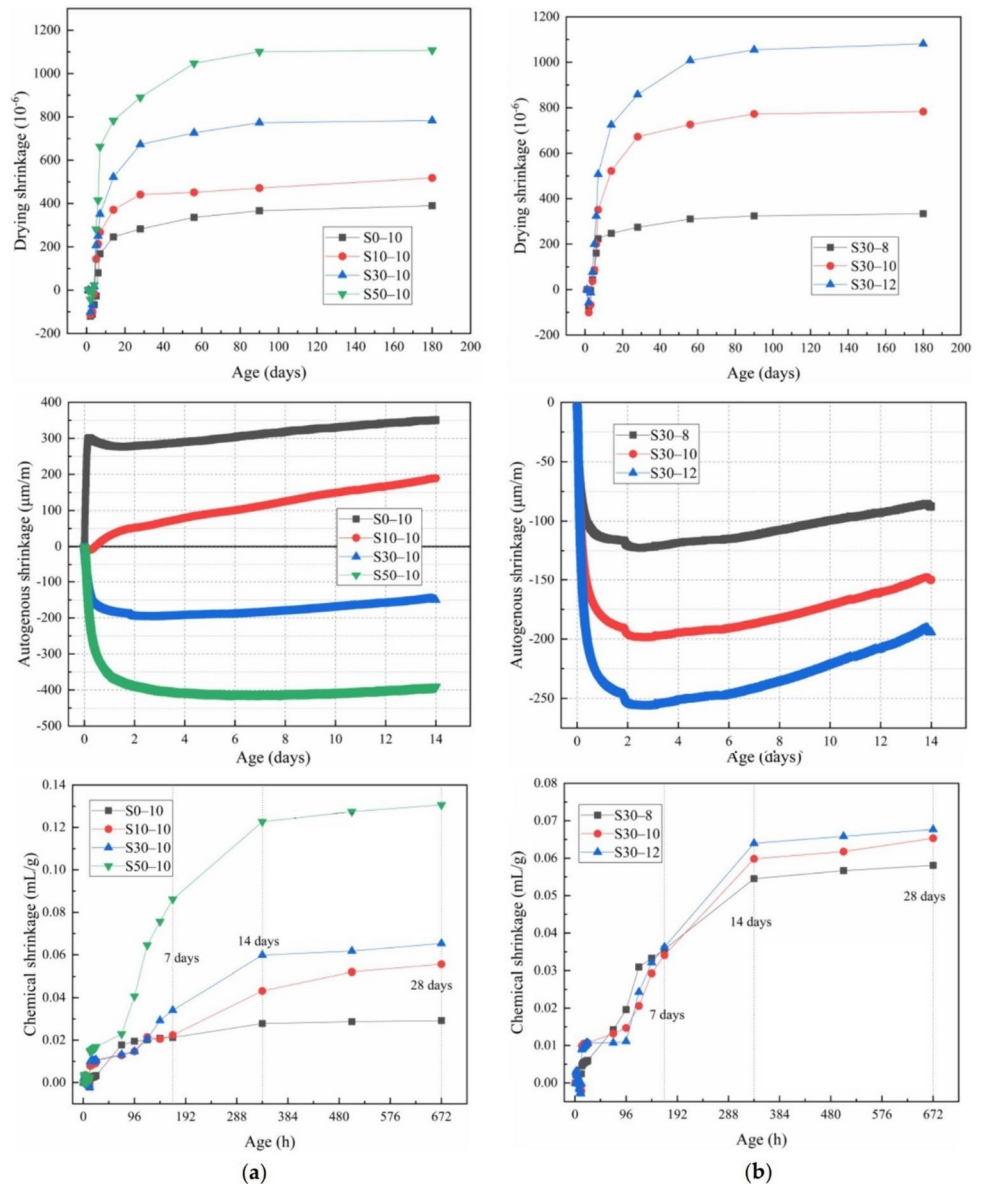
Understanding the causes of shrinkage is crucial to finding effective solutions to this problem. One of the leading causes of shrinkage in geopolymer and alkali-activated materials is the chemical reaction that occurs during the setting and hardening process. These materials are typically made by mixing an alkaline activator solution, such as sodium hydroxide or potassium hydroxide, with an aluminosilicate source, such as

slag, fly ash, or clay. This results in the formation of a three-dimensional network of geopolymeric gels that provide the strength and durability of the material [90, 91]. However, during the chemical reaction, water is consumed, which can result in shrinkage. Another factor that can contribute to shrinkage is the microstructure of the material. Geopolymer and alkali-activated materials have a unique microstructure different from traditional cement-based materials. In particular, geopolymer slurries cured at high temperatures result in higher chemical shrinkage than ordinary Portland cement [92]. The gel structure of these materials is more porous and has a higher surface area, which can lead to more shrinkage. Additionally, the pore size distribution and the presence of unreacted particles can also have an impact on the amount of shrinkage that occurs. A smaller critical pore size and a higher fraction of mesopores

(2.5–50 nm) result in a higher shrinkage [93]. An increment in the amount of slag and NaOH contributes to the pore structure of geopolymers, resulting in lower drying and autogenous shrinkage but higher chemical shrinkage, as seen in Fig. 5 [94].

There are several solutions to shrinkage in geopolymer and alkali-activated materials. One solution is to add certain additives, such as silica fume, to the mix [95]. These additives can help reduce the amount of water consumed during the chemical reaction, which can reduce shrinkage. The use of nanomaterials as additives in the mix, such as nanosilica, nanoalumina, and carbon nanotubes, has unique properties that can improve the microstructure of the material and reduce shrinkage [96, 97]. Another area of research is the usage of alternative aluminosilicate sources, such as rice husk ash and zeolite [98, 99]. These sources have the

Fig. 5 Effect of (a) slag (0–50%) and (b) NaOH content (8–12%) on the shrinkage results of geopolymers [94]



potential to reduce the carbon footprint of the material, as well as improve its durability and strength. Other additives, such as fibers, can help to improve the toughness and ductility of the material, which can reduce cracking [100, 101]. Curing done using various methods, such as steam curing, water curing, or ambient curing, is also an essential factor in reducing shrinkage [102, 103]. Proper curing can help to control the amount of water consumed during the chemical reaction. It can reduce the amount of drying shrinkage that occurs, as well as improve the durability and strength of the material [104, 105]. Mix design is also important in reducing shrinkage. The amount of alkaline activator solution, the type of aluminosilicate source, and the water content can all impact the shrinkage that occurs [106–108]. By optimizing the mix design, engineers and builders can reduce the amount of shrinkage that occurs and improve the durability and strength of the material. Another kind of shrinkage to be considered is that the geopolymer specimens demonstrate a significant volumetric shrinkage reaching 20% at exposure to elevated temperatures [109].

Fire resistance

While traditional cement-based concrete can spall and crack when exposed to high temperatures, reducing its ability to resist fire, geopolymers and alkali-activated materials have shown excellent fire resistance properties [110, 111]. One study found that geopolymer concrete had fire resistance without any exhibited spalling at various fire regimes compared to traditional concrete due to its high connected pore structure allowing water vapor escape [112]. Similarly, Duan et al. [113] exposed samples of geopolymer and OPC to temperatures of up to 1000 °C for several hours and found that geopolymers maintained their structural integrity and did not exhibit any signs of spalling, unlike the OPC samples. In fact, the desirable fire behavior are controlled by two opposite phenomena: (1) damage to the matrix due to thermal incompatibility of ingredients, and (2) further hydration or geopolymerization that densifies the matrix [114]. Le et al. [115] reported that up to 2 times, a significant improvement in strength can be achieved for geopolymer foams after exposure to a temperature of 1200 °C. These results suggest that geopolymers and alkali-activated materials have the potential to be used in a wide range of applications where fire resistance is a critical consideration. These include:

- Fire-resistant cladding and facades for buildings [116]
- Fire-resistant insulation materials [117]
- Fire-resistant coatings for steel structures [118]
- Fire-resistant flooring and paving materials [119]
- Fire-resistant radiation shields [11]

Many factors can affect the ability of geopolymers to resist fire. These include the type of precursor used, the type and concentration of activator used, fibers, and the curing conditions of the material [115, 120–123]. For example, the concentration of the activator used can also affect the material's fire resistance, with higher concentrations generally resulting in better fire resistance [120]. In addition, studies have shown that using slag as a precursor can decrease fire resistance compared to other types of precursors, such as fly ash [120, 124]. As documented by Luo et al. [125], a minor use (5%) of slag within siliceous (class F) fly ash-based geopolymers can cause higher crack intensities reaching five times in the matrix after exposure to elevated temperatures. To understand the fire resistance of geopolymers in detail, not only the crack density, crack rehabilitation, transformation of phase chemistry, and pore structure are needed further investigations [126, 127]. The loss in compressive strength of fly ash-based geopolymers can reach 65% by using slag instead of the siliceous precursor at elevated temperatures, as observed in Fig. 6 [125, 127]. Although a significant loss of compressive strength was observed with increasing slag content in the current literature, Junru et al. [128] reported that 100% slag-based geopolymer concrete has superior fire resistance than OPC concrete.

In addition to their fire resistance properties, geopolymers and alkali-activated materials also have several other desirable properties that make them a good choice for sustainable construction, including their low carbon footprint and

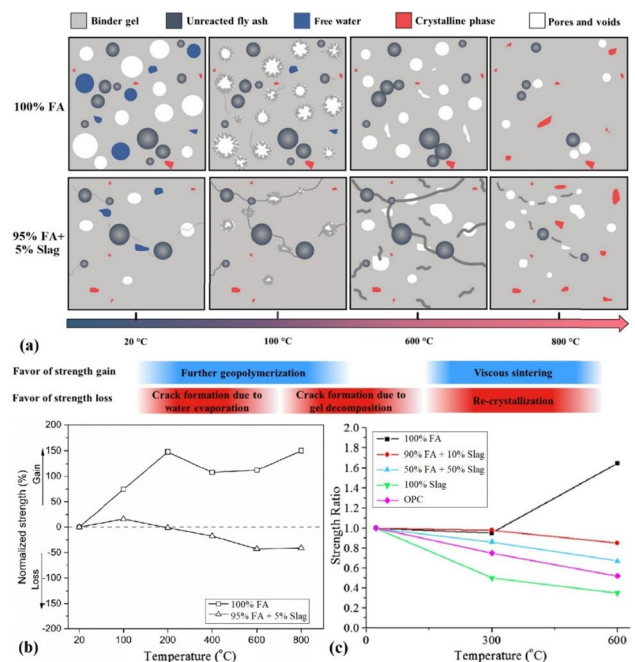


Fig. 6 The effect of slag on (a) matrix, on residual compressive strength of (b) 5% slag bearing specimens [125] and (c) specimens at various amounts of slag content [127]

high durability [14, 129]. While there is still much research and development needed to fully understand the potential of these materials, they offer a glimpse into a more sustainable and fire-resistant future for the construction industry.

Freeze–thaw resistance

In addition to superior durability and heat resistance, geopolymers' ability to resist freeze–thaw damage, a common problem that plagues conventional concrete and other building materials, is truly fascinating [130]. Before delving into how geopolymer resists freeze–thaw damage, it's essential to understand the effects of freeze–thaw cycles on traditional concrete. When water freezes in voids, it expands by about 9%, and this expansion exerts pressure on the surrounding materials. When this freeze–thaw cycle is repeated, the pressure becomes too much for the concrete to bear, and it begins to crack and break apart. This damage not only affects the appearance of the building but also weakens the structural integrity of the concrete. Once the concrete is damaged, it becomes more porous, allowing water to seep in and exacerbate the freeze–thaw cycle. This vicious cycle can lead to costly repairs, and in extreme cases, it can even lead to the total failure of the structures. In this respect, air-entraining admixtures are often studied in conventional concrete products [131]. Unlike OPC, these additives can impair the freeze–thaw performance of geopolymers [132, 133]. So, it is clear that finding a solution to this problem in a material scale is of utmost importance. Compared to low-calcium geopolymers, including fly ash and natural zeolite, slag-based geopolymers present better resistance to freeze–thaw cycles [123, 134, 135]. Slag-based concrete can withstand even after 300 freeze–thaw cycles [51]. This is possibly caused by their favorable pore structure in denser microstructure and high-strength matrix proportional to the slag content, as seen in Fig. 7.

Geopolymers are formed by the reaction between aluminosilicate and alkali solutions, which results in the formation of a three-dimensional network of Si–O–Al bonds [12]. This network is highly stable and resistant to both physical and chemical degradation [137]. One of the main reasons why geopolymer is able to resist freeze–thaw damage is its low permeability, as known in concrete technology [138]. Unlike cement paste, geopolymer has a much lower porosity, which means that it is less likely to absorb water [139]. When water does come into contact with the material, it is less likely to penetrate deep into the structure, and this reduces the risk of freeze–thaw damage. Another factor that contributes to the durability of geopolymer is its microstructure [136]. Geopolymer has a unique microstructure that is made up of a dense matrix of interlocking crystals. These crystals are tightly packed together, leaving very little space for

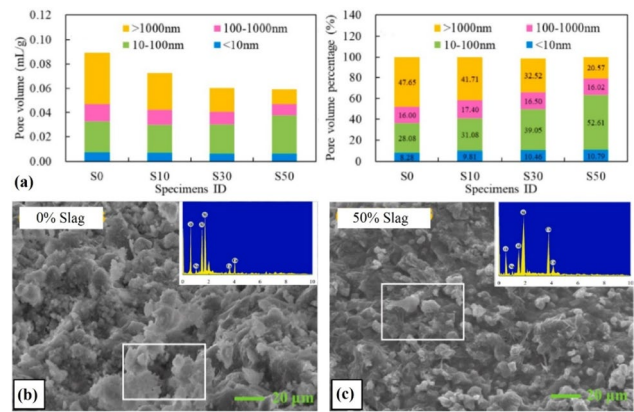


Fig. 7 Effect of slag content on (a) pore structure and microstructure of specimens, (b) without slag, and (c) with 50% slag [136]

water to seep in. This dense structure makes it difficult for water to penetrate the material, making it more resistant to freeze–thaw damage. The curing temperature of geopolymer is another factor that affects its ability to resist freeze–thaw damage [140]. Studies have shown that geopolymer cured at higher temperatures is more resistant to freeze–thaw damage than geopolymer cured at lower temperatures [141]. This is because higher curing temperatures result in a more compact microstructure, which makes it even more difficult for water to penetrate the material.

Resistance to aggressive solutions

The most aggressive challenges that traditional construction materials face are known as chloride permeability, sulfate, and acid attack for long-lasting performance [142]. While reported to be more resistant than OPC mortar [143], these degradation mechanisms are mostly also questioned for geopolymers as basic durability aspects to provide a comprehensive breakdown of how they are changing the game in the construction industry. The potential for use of geopolymer concrete in various applications worldwide has been investigated. In Australia, geopolymer mortar has been used in the construction of a wastewater treatment plant, where it has been found to provide superior resistance to chemical attack compared to sulphate-resistant traditional mortar [144]. In India, geopolymer concrete can be promising for constructing a bridge, high-rise buildings, highways, tunnels, dams, and hydraulic structures, to reduce the economic and environmental costs and natural resources, to utilize waste materials, to ensure long-life infrastructure construction, societal income, and employment generation compared to traditional concrete [145]. In Malaysia and Germany, geopolymer concrete has been used in the construction of tunnel segments, where it has been found to provide superior resistance to

sulphate and acid attacks and chloride ion ingress [146]. Overall, geopolymer concrete has been found to be a versatile and effective material for use in various construction projects.

Chlorides are commonly found in seawater, de-icing salts, and other sources, and they can penetrate concrete over time, leading to corrosion of embedded steel reinforcement. The corrosion statement can cause structural damage and shorten the lifespan of concrete structures [147]. Geopolymers, made from a combination of industrial waste and natural materials, have been found to be highly resistant to chloride penetration [148]. The structure of geopolymers is based on a three-dimensional network of covalently bonded tetrahedral units, which makes them highly resistant to water and chloride permeability. A chloride level of more than 0.07% by weight of concrete can be considered critical to initiate the corrosion of embedded steel [149]. Given this threshold chloride level in a certain depth (40 mm) of concrete, Tenakoon et al. [150] reported that it is required a significantly higher exposure time, reaching 21 times for high-volume slag-based geopolymer concrete compared to OPC concrete (please see Fig. 8). With increasing slag content, geopolymers have been found to have a low permeability to chloride ions, which means they are less susceptible to corrosion caused by chloride penetration [136]. The longer lifespan of geopolymers than traditional concrete reduces the need for frequent repairs and replacements [151]. This makes geopolymers an ideal material for use in coastal areas or other environments where chloride exposure is a concern.

In addition to chloride permeability, geopolymer products are also less susceptible to sulfate and acid attack compared to traditional cement products [152, 153]. Sulfate attack occurs when sulfate ions in water or soil react with the calcium hydroxide in concrete, forming calcium sulfate [154]. This can cause the concrete to expand and crack, leading to

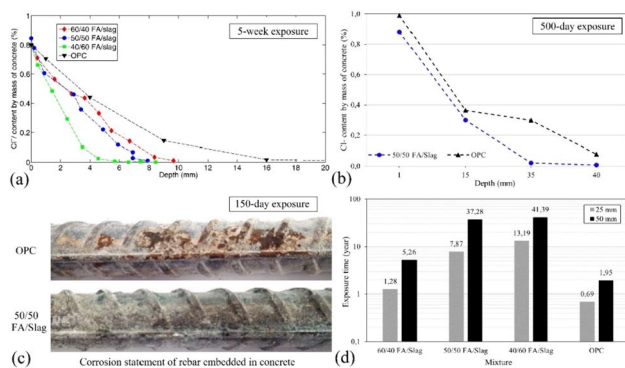


Fig. 8 Chloride content of various concrete series (a) at 5-week and (b) 500-day exposure time, (c) corrosion statement at 150-day exposure time, and (d) predicted service life (exposure time) of concrete series for chloride threshold level at 25- and 50-mm concrete depth [150]

structural damage [155]. Unlike cementitious composites, a better sulfate performance has been reported for geopolymers thanks to the contribution of sodium and magnesium sulfate solutions to a more stable cross-linked aluminosilicate polymer structure [156]. Compared to sodium sulfate, magnesium sulfate can cause higher strength losses, reaching ten times for slag-based geopolymers due to degradation of gypsum formation and transformation of C-A-S-H binding gels to non-cementitious and fibrous M-A-S-H products (please see Fig. 9) [157].

Acid attack occurs when acid rain or other acidic solutions come into contact with concrete, causing the surface to erode and weaken [158]. Geopolymers have been found to be highly resistant to both sulfate and acid attack [159]. This is because the chemical structure of geopolymers makes them less susceptible to chemical attack than OPC composites [153]. Using slag in geopolymers improves the pore structure, mass loss, and deterioration caused by acid attack, as seen in Fig. 10 [160]. These deteriorations are proportionally followed by strength loss of geopolymer composites. Overall, slag-based geopolymers have been found to provide superior protection against both sulfate and acid attack, making them an ideal material for use in harsh environments. While traditional concrete remains the most widely used material in construction, the superior performance of geopolymer concrete is making it an increasingly popular choice for sustainable and long-lasting infrastructure.

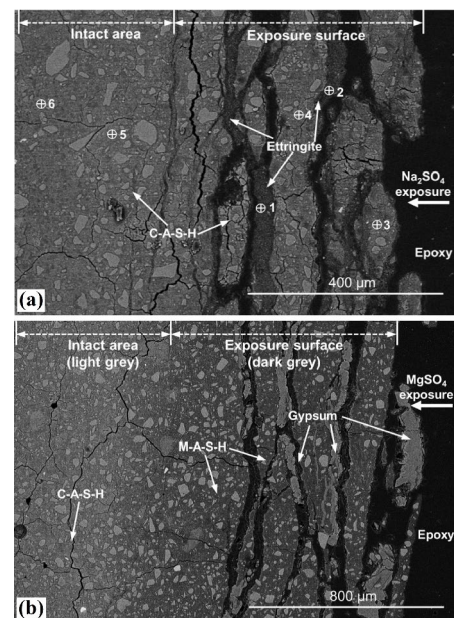


Fig. 9 The effect of (a) sodium and (b) magnesium sulfate on the microstructural deterioration of slag-based geopolymers [157]

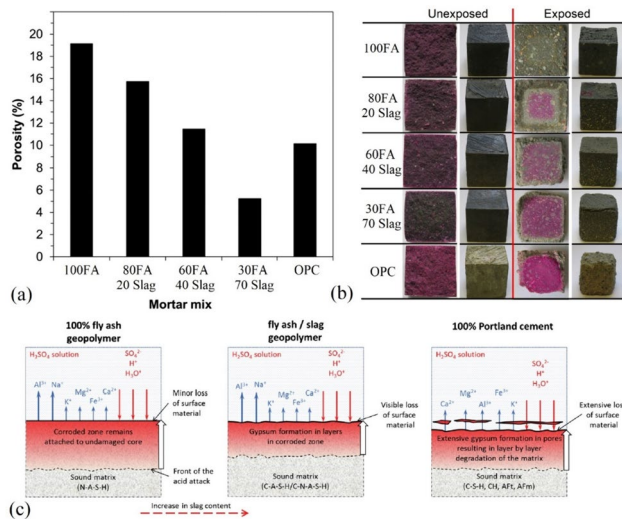


Fig. 10 Effect of slag content on (a) the porosity, (b) surface deterioration, and (c) the schematical deterioration mechanism of geopolymers [160]

Basic and recent approaches for improving durability aspects

The inherent complexity of alkali-activated materials can pose a major challenge in overcoming their poor durability aspects. Unlike its cementitious counterparts, it is not possible to improve these durability properties by controlling limited parameters such as water/cement ratio, binder dosage and binder type. The degradation mechanisms of these binders are significantly affected by many factors, including the mixing details, the type, chemistry, fineness, and amorphous content of precursors, the type and molarity of activator, silicate modulus, curing regime, pressing, etc. [28, 161–175]. Alkali-activated materials can be made into a more durable material by appropriate selection of precursors and alkaline activators, optimization of mixing ratios, and appropriate curing [176]. Enhancing the reactivity of aluminosilicates contributes to the development of geopolymeric network and strength [177]. SiO_2 and Al_2O_3 , the main components of zeolitic structures, are the most important oxides to be considered in geopolymerization [178]. For superior mechanical properties, it is recommended by many researchers that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio be in the range of 3.2–3.8 [179, 180]. In addition, a suitable CaO/SiO_2 ratio, which is mainly controlled by the slag ratio in the mixture precursors, can result in better durability of alkali-activated materials [54, 181]. A strong connection between strength and durability is expected due to the presence of stable reaction products in alkali-activated and geopolymer systems [182]. Therefore, all attempts increasing the strength can contribute the development of durability. Unlike

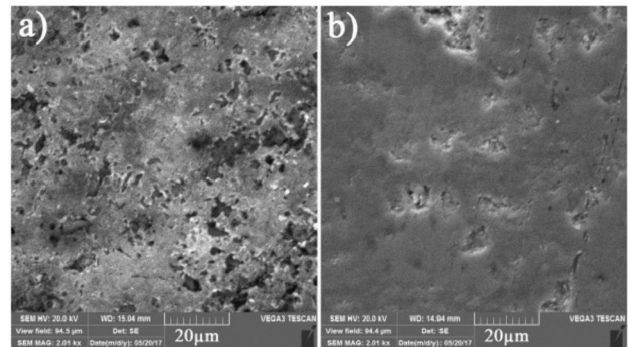


Fig. 11 Samples cured at (a) 110 °C (b) 400 °C for 30 min [186]

cementitious systems, threshold content of aggregate has been found to be a specific approach to increase the strength of geopolymer concrete [183]. This is probably due to the strong bond between the aggregate and the matrix [184]. The mechanical performance of geopolymers is related to their porosity structure. When a pre-setting pressure is applied to geopolymer mixtures, air bubbles are removed and macroporosity is significantly reduced, resulting in high mechanical strength [1]. Zivica et al. [185] developed a geopolymer material with low alkaline activator content by pressing the mixtures under 300 MPa pressure for 1 min. It was announced that 500 times higher mechanical results were obtained compared to the reference sample, and this increase was achieved by the decrease in porosity and pore size. Another parameter that affects this process with the hot press method is the temperature applied. As the applied temperature and application time increased, mechanical performances also increased. Ranjbar et al. [186] showed that samples with a compressive strength of up to 185 MPa were produced with a temperature between 110–400 °C and a pressing pressure of 74 MPa for a period of 10–40 min. In this application, it is understood that the microstructure improves significantly as the temperature increases from 110 °C to 400 °C (Fig. 11).

Recently, hot-pressed geopolymers have been introduced as a ceramic-like material that can be produced in a very short time, has a low amount of alkaline activator, and has high strength [187]. This method uses a simultaneous combination of continuous heating and pressing to eliminate the macropore structure, facilitate the dissolution of the reacted oxides, and accelerate the subsequent geopolymerization reaction. The material properties of hot-pressed geopolymers largely depend on the parameters of temperature, pressure and curing time. In a study, it was observed that increasing the temperature accelerated the dissolution of amorphous phases, the removal of water and the densification process of geopolymers [186]. The densification regarding the formation amount of geopolymer bonds under the influence of temperature and pressure parameters is visually presented in Fig. 12.

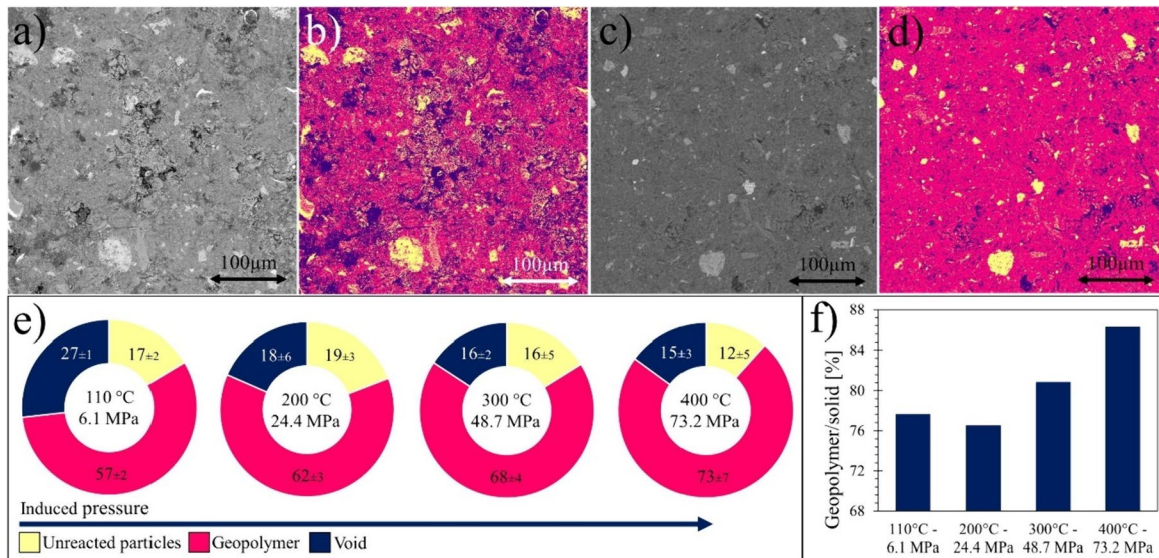


Fig. 12 Image analysis of the hot-pressed geopolymer produced at (a) and (b) 110 °C-6.1 MPa, (c) and (d) 400 °C-73.2 MPa; (e) phase distribution of the specimens processed at 110 °C-6.1 MPa,

200 °C-24.4 MPa, 300 °C-48.7 MPa, and 350 °C-73.2 MPa; and (f) geopolymer gel to solid ratio [188]

Conclusions and future perspective

As the demand for sustainable and low-carbon footprint materials continues to grow, it seems important that we continue to innovate and advance the science of geopolymers and alkali-activated materials. Recently, a lot of research has been done on the durability of these materials to great success. However, compared with the current progress of ordinary Portland cement, there is still a lot of work to be done in the coming years to overcome inherent problems and difficulties. The following conclusions and future recommendations can be drawn from this critical review on the durability of slag-based alkali-activated materials:

- The complexity in durability of alkali-activated systems appears by researchers as the most significant obstacle to becoming commercial-off-the-shelf products of them. Mechanical loss, a quantitative indicator for durability, is mostly used in order to evaluate the degradation level of alkali-activated and geopolymer systems. However, overcoming durability deficiencies is not as easy to manage as mechanical aspects because of complex chemistry, strongly affected by many factors, including compositional details, curing regimes, pre-setting pressure, environmental degradation mechanisms, etc. For this reason, recently, durability studies have come to the fore in research rather than their mechanical, cost and environmental properties.
- Inappropriate design of these systems can cause dimensional stability problems, including micro and macro cracks that appear during setting and hardening. Therefore, unbound

and dissolved alkalis (Na and K) and calcium ions in the matrix are easily leached and carbonated. Not only is durability compromised by the dissolution of the aluminosilicate gel and free alkaline ions during leaching, but the alkali-activated materials may also pose a further threat to the environment as it contains high volumes of industrial byproducts with concentrated toxic heavy metal contents. When specimens are exposed to water, leaching of sodium silicate can produce a strength loss of up to 25%, while interruption of geopolymeric reactions by evaporation of water can result in a higher strength loss of up to 69% due to the increased porosity (around 50%) of the solid body. A high concentration of alkalis is required for favorable strength development of alkali-activated materials. However, their increased solubility and absorption rate of CO₂ accelerate efflorescence. An increment of slag content instead of fly ash contributes to the carbonation resistance of them, and even some extent improvement in strength can be achieved at various carbonation exposures.

- One of the main reasons for shrinkage in geopolymer and alkali-activated materials is the chemical reaction that occurs during the setting and hardening process. Water is consumed during the chemical reaction, which can cause shrinkage. Another factor that can contribute to shrinkage is the microstructure of the material. The gel structure of these materials is more porous and has a higher surface area than OPC, which can lead to greater shrinkage. The increase in the amount of slag and NaOH contributes to the pore structure of alkali-activated materials, resulting in lower drying and

autogenous shrinkage but higher chemical shrinkage. By optimizing the mix design, engineers and builders can reduce the amount of shrinkage and improve the durability and strength of the material.

- These materials are fire resistant without showing any spalling in various fire regimes compared to conventional concrete, due to the highly interconnected pore structure that allows water vapor to escape. Alkali-activated materials exposed to temperatures of up to 1000 °C for several hours can maintain their structural integrity and show no signs of spalling, unlike OPC samples. Current results demonstrate that geopolymers and alkali-activated materials have the potential to be used in a wide variety of applications where fire resistance is critical: (1) fire-resistant cladding and facades for buildings, (2) fire-resistant insulation materials, (3) fire-resistant coatings for steel structures, (4) fire-resistant flooring and paving materials, and (5) fire-resistant radiation shields. Studies show that the use of slag as a precursor can lead to a decrease in fire resistance compared to other types of precursors, such as fly ash. Even the use of small amounts (5%) of slag in siliceous fly ash-based materials can cause higher crack densities in the matrix, up to fivefold, after exposure to high temperatures. To understand the fire resistance of alkali-activated materials in detail, further research is needed not only on topics such as crack density, crack rehabilitation, transformation of phase chemistry, and pore structure.
- Unlike OPC, air-entraining admixtures can impair the freeze–thaw performance of alkali-activated materials. Therefore, it is clear that finding a solution to this problem at a material scale is of utmost importance. Compared to low-calcium ones, including fly ash and natural zeolite, slag-based materials have better resistance to freeze–thaw cycles. This is probably due to suitable pore structures with denser microstructure and high strength matrix proportional to the slag content. One of the main reasons why these materials are resistant to freeze–thaw damage is their low permeability, as is known in concrete technology. Unlike cement paste, alkali-activated materials have much lower porosity, meaning they are less likely to absorb water. Another factor is a unique microstructure consisting of a dense matrix of interlocking crystals. These crystals are packed tightly together, leaving little space for water to seep in. This dense structure makes it harder for water to penetrate the material, making it more resistant to freeze–thaw damage.
- These degradation mechanisms examined in the article are mostly interrogated as key durability considerations for alkali-activated materials to provide a comprehensive breakdown of how they are changing the game in the construction industry. Overall, it is understood that this concrete

will be a versatile and effective material for use in a variety of construction projects, such as wastewater treatment plants, bridges, high-rise buildings, highways, tunnels, dams, hydraulic structures, and tunnel segments. A higher exposure time of up to 21 times is reported for high-volume slag-based material concrete compared to OPC concrete in terms of threshold chloride level. With increasing slag content, these materials were found to have lower permeability to chloride ions; this means they are less susceptible to corrosion caused by chloride penetration. This makes alkali-activated materials an ideal material for use in coastal areas or other environments where chloride exposure is a concern. Unlike cementitious composites, a better sulfate performance has been reported for these materials, thanks to the contribution of sodium and magnesium sulfate solutions to a more stable cross-linked aluminosilicate polymer structure. Compared to sodium sulfate, magnesium sulfate can cause higher strength losses, up to tenfold for slag-based materials due to the degradation of gypsum formation and transformation of C-A-S-H binding gels to non-cementitious and fibrous M-A-S-H products. The favorable chemical structure of alkali-activated materials makes them less susceptible to chemical attack than OPC composites. The use of slag improves the pore structure, mass loss, and deterioration caused by acid attack. In general, slag-based materials have been found to provide superior protection against both sulfate and acid attack, making them an ideal material for use in harsh environments.

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Declarations

Conflict of interest The author has no relevant financial or non-financial interests to disclose.

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