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BOOK REVIEW

Durability Properties of Alkali Activated Slag Composites: Short Overview

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Abstract

Despite the advances in studies utilizing industrial, construction and agricultural wastes as alternative materials for concrete making, there are still gaps to be covered on the durability characteristics of most materials. This study presents a shot overview on the durability properties of alkali-activated slag (AAS) composites. The durability properties of AAS explored include permeability, alkali silica reaction, carbonation, freeze and thaw, fire resistance, corrosion, and resistance to sulphate, chloride and acid attacks. The research outcomes indicated that AAS possessed strong durability characteristics in terms of resistance to acid and sulphate attacks, however, areas such as permeability, alkali silica reaction, carbonation and freeze-thaw resistance, have not been overly explored. A general overview of the performance and limitations of AAS has been provided, and the study suggested specific areas for further investigations. The information provided in this study will be useful for users of AAS, and pave way for innovative researches on AAS composite.

Keywords Alkali activated slag · Cement · Concrete · Durability · Hydration mechanism

1 Introduction

The sustainability approach, focussing on green consumption of discarded materials and suppressing climate change, is an appropriate solution to environmental degradation. Thus, there is a systematic development of new products from the routinely generated wastes from both industrial and construction activities. Over the last few decades, sustainable cementitious composites were proposed in several studies [1–6], covering the use of recycled construction materials, and naturally sourced and synthetic materials [7]. Through the research developments, minimization of carbon foot print and reducing cost of concrete production is the overall goal, however, Ordinary Portland Cement (OPC) composite, which produces huge carbon emission, are found irreplaceable, until the introduction of alkali activated materials (AAM) and geopolymers.

A comparison between AAM and OPC mortar/concrete is described in Table 1. For environmental friendliness and economic concerns on production of mortar or concrete, alkali activated materials (AAM) are considered as a better alternative to OPC. Also, in terms of mechanical and durability behaviour, AAM based composite are found somewhat above OPC mixture. The production of the latter results in the emission of toxic substances that pollute the atmosphere. According to several studies [18–20], about one tonne of carbon dioxide is emitted into the atmosphere during production of a tonne of Portland cement. However, AAM, usually produced by using an activator (mostly sodium-based compounds) to enhance the binding quality of a supplementary cementitious material, is more prominent, in that it renders less green house effect on the environment, and with reduced energy and water consumption.

The most common AAM is the alkali-activated slag (AAS). However, other AAMs are such as fly ash, metakaolin, and glass based [21–24], and other by-products [25–27]. Several investigations involving the use of AAS have revealed numerous mechanical and durability properties of composites incorporating AAS. When AAS was utilized as a binding agent in pervious concrete [28], it was reported that both the mechanical and permeability properties of the concrete were enhanced. The influence of the activator, in terms of high

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Table 1 Comparison of AAM to OPC in terms of mechanical and durability properties

Properties	Binders		Precursor materials	Sources
	AAM	OPC		
Tensile strain	High	Low	Slag, fly ash	[8]
Splitting tensile strength	High	Low	Slag, fly ash	[8]
Early strength	High	Low	Fly ash	[9]
Tensile strength	High	Low	Slag	[10]
Flexural strength	Poor	Poor	Slag	[11]
Modulus of elasticity	Low	Moderate	Fly ash	[12]
Bond to reinforcement steel	Same level	Same level	Fly ash	[13]
Fracture energy	High	Low	Slag	[14]
Drying shrinkage	High	Moderate	Slag	[15]
Sulphate attack resistance in 5% Na_2SO_4	Lower strength reduction after 60 days of exposure	Higher strength reduction after 60 days of exposure	Slag	[16]
Sulphate attack resistance in 5% $MgSO_4$	17% strength loss after 12 months' exposure	25% strength loss after 12 months' exposure	Slag	[16]
Exposure to acetic acid	Retained 75% of original strength after 150 days of exposure	Retained lesser strength than AAM after 150 days	Slag	[17]
Interfacial Transition Zone (ITZ)	Denser	Less dense	Slag	[14]

alkalinity, of the composites, could be major contributors to the behaviour of AAS. However, other factors such as, mix design and duration of mixing AAS concrete constituent materials, have been identified as factors that also affects AAS fresh and hardened state properties [29, 30].

In evaluating the durability of AAS composite, due attention is required to identify relevant tests to be performed to avoid counter-action of activators. Moreover, a study conducted by Thunuguntla and Rao [31], revealed that, durability tests involving the use of chemical attacks with sodium or magnesium compounds, might not show significant deterioration effects. In effect, mediums such as made up of sodium chloride, sodium sulphate and magnesium sulphate are likely to enhance the mechanical properties of the composite than cause major defects.

While there are numerous researchers that examined the durability of AAS composite, however, it is worthy of note that many irregularities are associated with AAS. Therefore, this study, based on literature review and practical judgments, evaluates the durability issues relating to AAS composites. The result of this study would help suggest possible solutions to the identified setbacks in the development of AAS, and open paths for further studies in this field.

2 Durability of Alkali Activated Slag

The resistance of AAS composite against aggressive environmental conditions is one major factor to be checked prior to its full adoption. While there are research efforts relating to the AAS durability, yet the process of improving this innovative material still requires further checks. Studies [21, 32, 33] have shown that the reaction product of alkali-activated slag, among other factors, contributes to its durability property. In this section, different types of deterioration mechanism as a measure of the durability of AAS are further considered.

2.1 Permeability

Permeability of binder/concrete is one of the major factors that determines its durability. During design, adequate measures are mostly taken to ensure that the concrete is less permeable as much as possible.

Several studies have shown that AAS has a lower permeability compared to ordinary Portland cement (OPC) concrete [34, 35]. However, some other studies also found that AAS is more permeable compared to OPC [28, 36]. When AAS composite is highly permeable, compared to OPC, it might be as a result of microcracks developed following inadequate predrying of the matrix [37]. On the other hand, the impermeability of AAS compared to OPC is one of the reason it has been used for radioactive waste encapsulation, as it prevents the waste from getting to the environment. Owing to the variance in the view of researchers, further investigations are necessary to ascertain factors that alter permeability of AAS composite. Different admixtures or micro filling nano materials may be dosed with the AAS mixture to possibly enhance its pore structures. Variation of water permeability value with alkaline solution/slag content in AAM is shown in Fig. 1, and chloride permeability with alkaline solution/slag content is presented in

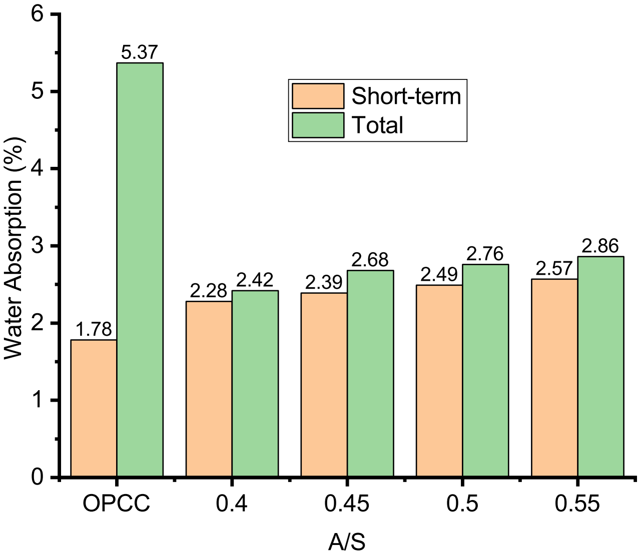


Fig. 1 effect of alkaline solution-slag ratio on the permeability of AAM composite. Adapted from [39]

Fig. 2. Experimental set-up of permeability test based on Darcy method is shown in Fig. 3. The study by Behfarnia [39] established that 0.45 alkaline solution/ slag content ratio is the optimum.

Bernal [36] suggested that increasing the slag content in AAS could lead to significant decrease in the capillary sorptivity. Similar observation was made by Rodriguez et al. [40], where it was reported that permeability and total porosity were reduced when the slag content was increased from 300 kg/m^3 to 400 kg/m^3 in an AAS mixtures. However, when the slag content was increased to 5000 kg/m^3, the authors reported that there was no significant change was observed in the permeability of the AAS. In another related study, a replacement of 10% slag with micro-silica has been found to improve the impermeability of AAS [41], which was attributed to the effect of additional reaction product and particle of the system, leading to a more densified microstructure.

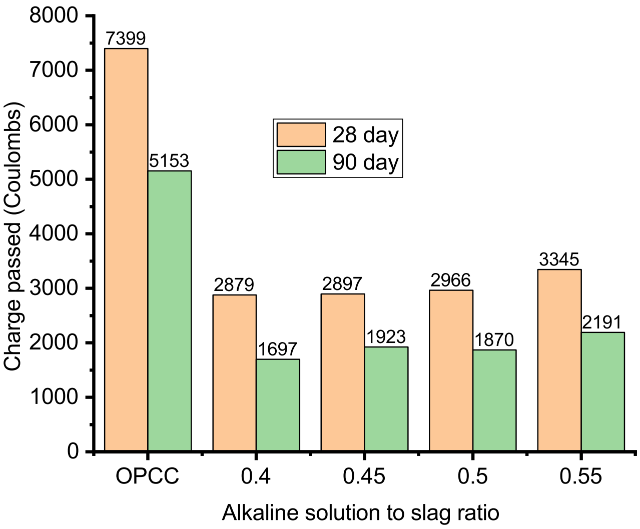


Fig. 2 rapid chloride permeability (in terms of charge passed) with alkaline solution/ slag content. Adapted from [39]

Slag has been suggested for enhancing pore structures of AAS composite, by the activity of the hydration product. However, the mechanism of the slag application is still ill defined. Therefore, a more detailed experimental design and optimization of the slag content required for AAS matrix development is required.

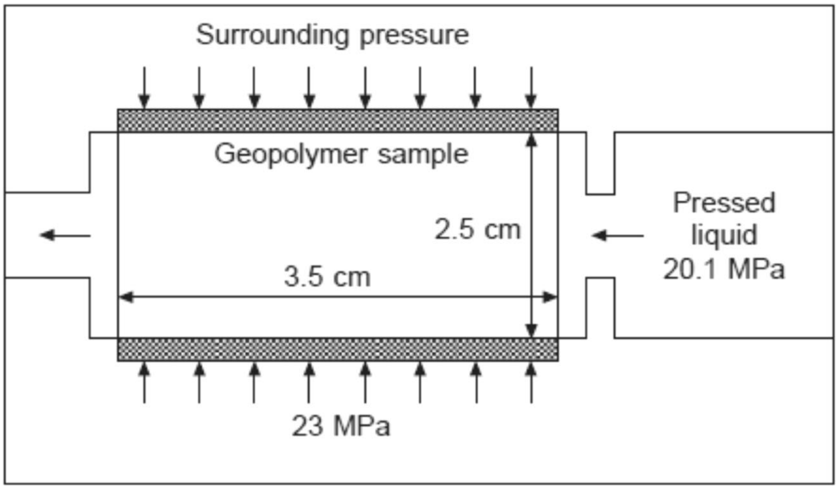
2.2 Sulphate Attack

One of the common threats to concrete's durability is sulphate attack. This attack occurs when concrete is placed in areas with high amount of sulphate in the soil, or constant contact with other sulphuric sources. Earlier studies [42–44] have shown that sulphate attack can lead to several deteriorating effects in concrete, such as cracking, expansion, spalling, and strength loss. Sulphate attack can be classified into physical and chemical sulphate attack based on the mode at which it deteriorates the concrete.

It has been generally accepted that chemical sulphate attack is eminent in concrete made with 100% Portland cement due to high amount of its C_3A content [45]. However, with the absence of C_3A content in AAS, it is expected that its resistance would differ. Based on the studies, it is clear that AAS have high resistance to sulphate attack. A study [46], showed that compressive strength of AAS samples stored in 1–2% magnesium sulphate solution increased after 1 year, and no significant decrease for the following 2 years. However, similar OPC samples in the solution deteriorated significantly within 6 months. Figures 4 and 5 present the effects of sodium and magnesium sulphates, respectively, on the compressive strength of alkali activated composite.

Also, loss in compressive strength was found to be insignificant when AAS concrete was soaked in 5% sodium sulphate for 90, while samples made with OPC had a loss of about 43% [40]. In addition, according to the authors [40, 46], samples made with OPC were severely damaged after few days, and also experienced expansions up to 6 times than AAS composite. The deterioration of samples made with OPC can be attributed to gypsum and ettringite formation. However, Komljenovic et al. [43] attributed the better resistance of AAS samples to the presence of aluminate ions and absence of calcium hydroxide, which prevents the formation of gypsum and ettringite. Also, AAS, when activated using sodium sulphate, exhibits enhanced durability compared to OPC when immersed in 5% magnesium sulphate [47]. The sulphate penetration rate of AAS activated with sodium sulphate reduced with increase in curing age. This may be due to the formation of hydrated pores fillers. However, deterioration of sodium sulphate activated slag was observed when the samples were exposed to 10% magnesium sulphate solution

Fig. 3 Permeability test set-up and test of AAM using Darcy method. Adapted from Zhang et al. [38]



[48]. In addition, higher strength loss was observed compared to that of OPC. The high strength loss has been attributed to the formation of magnesium silicate hydrate (M-S-H) and gypsum as a result of interaction between the magnesium ions and calcium silicate hydrate (C-S-H). This assertion was corroborated in a related study [49]. A further assessment of sulphate attack on AAS composite when it is altered with mineral admixtures is required. Obviously, mineral admixtures are bound to influence the hydration phenomenon and pore structures.

2.3 Alkali Silica Reaction (ASR)

Though slag is used in OPC concrete to curb the expansions due to ASR, there is no consensus yet about the resistance of AAS made with ASR reactive aggregates. With the high slag and directly calcium content in AAS, it is expected that AAS should be resistant to alkali ASR. However, Bakharev et al. [50] found out the resistance of AAS to ASR is lower to that of OPC composites. Expansions were observed in AAS samples during the tests, and it was attributed to the formation of sodium calcium silicate hydrate [51].

Regulations for ASR requires that sodium oxide equivalent is lower than 0.8% in OPC. However, AAS contain higher sodium oxide because of the activators used, therefore it could be more susceptible to alkali silica reaction. Some studies have observed that AAS is resistant to ASR, and this resistance has been attributed to the most alkalis in the pore solution being bounded to the hydration products. Therefore, there's insufficient alkali to dissolve the silica in the reactive aggregates [52]. However, there is no convincing proof of this, as there is no full understanding of how this happens, and the extent or amount of alkali bounded to hydration products.

2.4 Acid Attack

Alkali activated slag is known to posses high resistance to acid attack compared to OPC [53]. Another study also affirm this assertion [54], where they stored the samples in hydrochloric and tetraoxosulphate(IV) acids of pH 2. However, AAS still

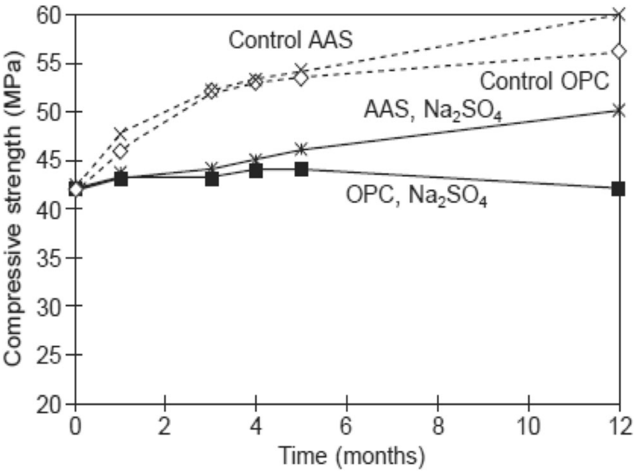


Fig. 4 Effect of sodium sulphate (Na_2SO_4) exposure on compressive strength of AAS and OPC mixture [42]

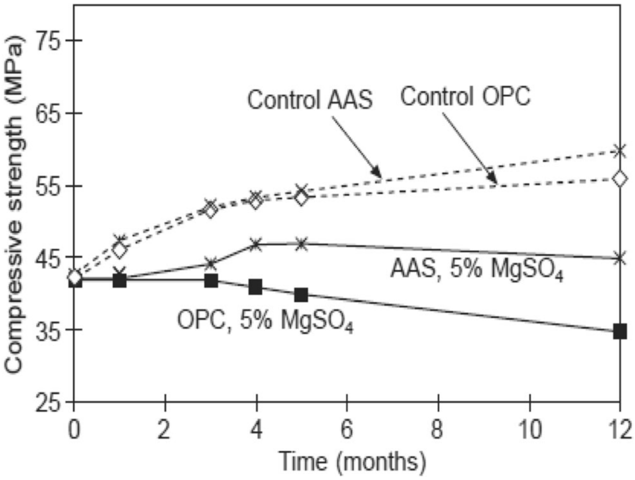


Fig. 5 Effect of magnesium sulphate ($MgSO_4$) exposure on compressive strength of AAS and OPC mixture [42]

deteriorates in these acidic environments. The acid resistance of concrete is essential because concrete structures in mining, mineral processing and chemical industries are exposed to acid attack. Overall, AAS is rated as more acid resistance than OPC, mainly because of its low calcium content.

2.5 Chloride Attack

Penetration of chloride ions into the concrete is mainly responsible for the corrosion of reinforcements [55–57]. Chloride ions get in contact with concrete from sources such as sea water and de-icing salts used in winter seasons. Figure 6 shows the rapid chloride penetration tests set-up. Based on the ASTM C1202 criteria, current (I) transmitted through a concrete slab by an external voltage (60 V) is measured. Thus, a curve of current versus time obtained at intervals 0, 30 and 360 min, is plotted, and integrated to through the period of test to determine the charge passed (coulombs). Table 2 shows the description of chloride penetration rate in terms the of charges.

Though the conventional rapid chloride penetration test (RCPT) used for OPC concrete has been found to be unsuitable for AAS. The results obtained from the test showed that AAS concrete have lower chloride diffusion coefficient compared to OPC concrete [34]. Also, better chloride resistance has been observed in AAS concrete subjected to chloride ion sources [59]. This enhanced resistance has been attributed to its pore structure [60], and gel composition [37]. Slag activated with calcium carbonate showed higher chloride resistance compared to those activated with alkali earth hydroxide (i.e. sodium hydroxide and potassium hydroxide). This higher resistance has been attributed to the reaction of the calcium hydroxide with chloride ions in the system to form calcium hypochlorite (Ca (ClO_2)). The formation of this new products reduced the concentration of the alkali in the system [61]. Higher resistance of AAS concrete compared to OPC concrete has been attributed to the absence of calcium hydroxide in AAS [62]. This observation correlates to lower diffusion coefficient observed in AAS [37].

2.6 Carbonation

The penetration of the carbon dioxide from the atmosphere into the concrete leads to concrete degradation. Carbon dioxide attacks the calcium components in concrete and converts it into calcium carbonate, thereby lowering its pore solution alkalinity. Lower alkalinity in concrete leads to corrosion of the embedded reinforcement. It is understood that a concrete with lower permeability can resist the carbonation process as it lowers carbon dioxide penetration rates. Moisture at an optimal level is required for this reaction to occur in concrete. Too much supply of moisture to the concrete prevents the concrete from carbonation, and too low supply of water would also protect the concrete against carbonation as there won't be enough water to dissolve the carbon dioxide. An experimental set-up for accelerated carbonation test by application of pressure is shown in Fig. 7. As can be seen, accelerated carbonation test vessel comprise of a pressure Aging Vessel, which is for simulating long term aging of the composite. A CO_2 cylinder s used so as to supply the vessel with a 100% CO_2 concentration and at a pressure of 2.8 bars. In the test set-up, three 60 mm sample discs are present, from which one sample can be utilized for monitoring the progress of carbonation based on phenolphthalein indicator. But, two other samples are left inside the vessel until a full carbonation is achieved. It is to be noted that full carbonation achievement can vary depending on number of days.

To evaluate the carbonation of concrete, two factors has to be observed; the rate of carbonation and the coefficient of carbonation. He et al. [64] observed that the strength of the AAS is related to its resistance to carbonation. According to the authors, a concrete with compressive strength less than 30 MPa undergo rapid carbonation, which might lead to slight reduction in strength. However, AAS in the compressive

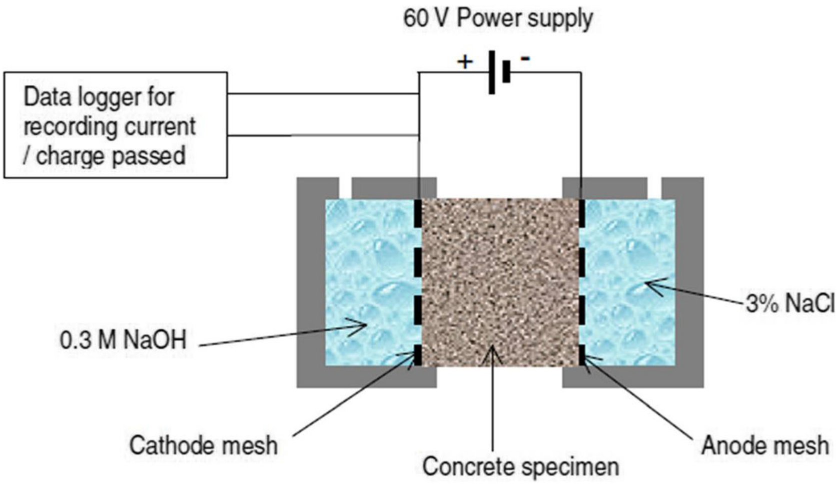


Fig. 6 Rapid chloride penetration test. Adapted from ASTM C1202 [58]

Table 2 chloride penetration rate as per ASTM C1202

Charge	Chloride ion penetration
>4000	High
2000–4000	Modrate
1000–2000	low
100–1000	Very low
< 100	Negligible

strength range of 30 MPa to 50 MPa undergo less carbonation, and there's no significant strength loss. Also, AAS with compressive strength higher than 50 MPa was found to undergo no carbonation.

Bakharev et al. [50] found out the rate of carbonation of AAS is faster than that of OPC when both binders were evaluated with the accelerated carbonation test. However, the rate of carbonation of AAS is only slightly faster than that of OPC when they undergo natural carbonation. Also, it was found out carbonation deterioration mechanism is different in AAS. An example is when the dissolved CO_2 reacts with the C-S-H in AAM thereby reducing the pH of the solution. This reduction in the alkalinity of the pore solution leads to loss of passivation thereby exposing reinforcement to corrosion [65]. These studies concluded that using accelerated carbonation tests used for OPC to evaluate AAS does not represents accurately the carbonation of AAS.

Increasing the slag content can be used to reduce the rate of carbon dioxide penetration into AAS [40], as a result of a more densified microstructure [66]. However, after a slag content above 400 kg/m^3, the water to binder ratio has a more significant effect on the rate of carbon dioxide penetration. This is because of self-desiccation, which leads to micro cracks in AAS. Therefore, it is critical to ensure that an optimized slag content is used for AAS. The type of activator has also been found to affect the carbonation of AAS. Activation of slag with sodium carbonate showed higher carbonation compared to those activated with sodium silicate [67].

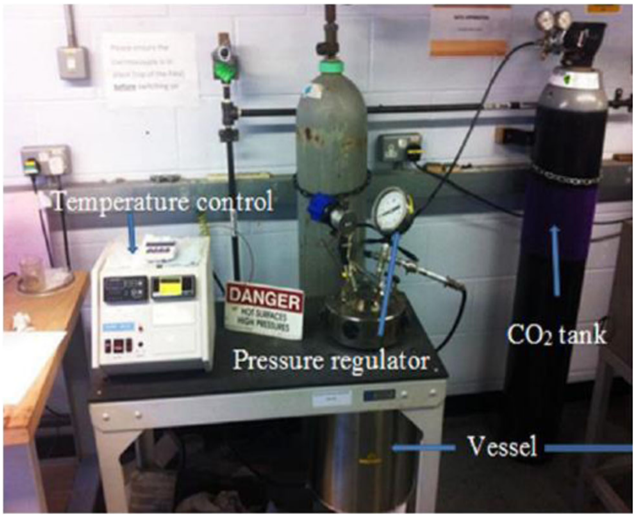


Fig. 7 Accelerated carbonation test (pressurized). Adapted from [63]

The main carbonation products in AAS have been identified as aragonite, calcite and vaterite [68]. In cases of low alkalinity of the pore solution, trona might be formed and natron formation when the pore solution alkalinity is high [69]. The additional formation of trona and natron shows the effect of the concentration of the activator used on the carbonation mechanism. Decrease in the concentration of sodium silicate from 7% to 3% has been found to increase carbonation [70]. When AAS was subjected to carbonation at different relative humidity (RH) levels, it was observed that the highest carbonation occurred at 50% RH [71].

2.7 Freeze and Thaw Resistance

The ability of concrete to resist deterioration due to the freeze and thaw cycle (frost in cold regions) is referred to as freeze and thaw resistance. Freeze and thaw is detrimental to concrete, as it leads to internal cracks, expansion, and mass loss [72]. This phenomenon of freeze and thaw can be more pronounce in AAM based composites, due to its porous nature. Thus, the internal and external structure of AAS composite can be modified, due to micro-disintegration of grains. But, it is possible that concrete resistance to freeze and thaw can be improved by using air entrained admixtures. Currently, there are no significant effect of freeze and thaw reported on AAS incorporating air entrained admixture. According to Pacheco-Torgal [73], AAS composites exposed to freeze and thaw only showed some scaling after 40 cycles, but other mixtures not having air entrainer did not show any scaling at the same number of cycles. The high concentration of electrolyte in the pore solution of AAS and low water demand ensures that AAS is resistant to freeze and thaw cycle [73]. This high resistance of AAS to freeze and thawing was observed in samples without air entrainers, compared to OPC samples, which passed less than 300 cycles before deteriorating [74]. The addition of air entraining admixture may also influence strength increment in AAS concrete. It has also been reported that no deterioration or weight loss occur in AAS samples with high compressive strength when exposed to freeze and thaw cycles [75]. However, despite AAS activated with sodium sulphate showing higher strength, but its performance under freezing and thawing cycles requires further investigation. In recent studies, addition of materials such as nano silica, nano alumina, and nano clay [74] or glass wastes [22] to AAS concrete has been reported as a suitable means of reducing compressive strength loss due to freeze and thaw. For the glass based AAS, insolubility of glass aided the improvement in resistance of AAS concrete to freeze and thaw.

2.8 Resistance to Reinforcement Corrosion

Corrosion generally reduces the structural integrity of concrete [76]. The resistance of reinforcement inside concrete to corrosion is dependent on the alkalinity of the pore water solution and permeability of the matrix. The alkalinity in the pore solution of concrete is mainly affected by chloride ingression [77, 78]. The chloride ions do not directly affects the embedded reinforcement, but the ions lowers the alkalinity of the pore system, thereby causing a depassivation which leads to corrosion of the reinforcements [37]. As the permeability of AAS is very low compared to that of OPC, the movement of the chloride ion into the pore system is restricted thereby preventing the lowering of the alkalinity of the pore solution [79]. It is also shown from the study that reinforced AAS concrete stored in seawater, showed no sign of corrosion after 1-year storage. According to Babee [80], alkali activated mortars possess better half-cell potential and polarization resistance than OPC mortars, when tested in a passive condition. AAM mortars, due to its higher alkalinity than OPC, possesses greater resistance to steel corrosion [81]. While alkalinity of AAM is the catalyst to its high corrosion resistance, yet uncertainties associated with different types of precursor used in AMM composite can be further explored in the future.

Weight loss of 0.18% - 0.37% was observed in reinforced AAS concrete samples after 48–75 cycles tested under the accelerated method which involves repeated wetting-drying cycles [30]. However, OPC in the same strength class experienced a weight loss of 1.9% after undergoing 45 cycles.

2.9 Fire Resistance

Predominantly, concrete in all forms have good resistance to fire. Convectional concrete degrades and decomposes at temperatures higher than 800 °C. The decomposition of the concrete is as a result of destruction and loss of moisture from the crystalline hydrates including C – S – H and other components of the concrete. This results in spalling of hot concrete layers from the cooler layers [82, 83], and to a certain extent, concrete cover to reinforcement protects the embedded steel in concrete [84]. In AAS, nano pores are present in its microstructure, which provides a pathway for the movement of bonded water to leave the concrete. These nano pores allow the moisture to leave the concrete at extreme temperature without causing any destruction to the aluminosilicate network [85]. AAS have a lower temperature gradient within its body compared to conventional concrete as heat transfers faster in alkali activated concrete when exposed to fire [86]. This is majorly because AAM stores large quantity of moisture in its pore structure, thereby making it endothermic in nature [87].

Similarly, Li [88] observed that when alkali activated concrete is exposed to elevated temperature in the range of 800 °C to 1000 °C, there was minor cracks on the concrete but no spalling. However, in convectional concrete exposed to the same temperature range, wide surface cracks were observed, coupled with severe spalling.

2.10 Efflorescence

The whitish deposits formed on the surface of some AAS samples is called efflorescence. Efflorescence occurs as a result of leaching out of water which contains free alkali from the samples. After the leaching of the free alkali with water, the alkali reacts with the surrounding carbon dioxide to form the whitish alkali carbonate. Some possibility of the formation of alkali sulphate is also possible [89]. Small quantity of efflorescence on the surface of AAS sample or structure is not a threat to its durability and strength. However, when a higher quantity is formed due to certain types of activators used or curing condition employed, the AAS integrity might be breached. Higher quantity of efflorescence on the surface of AAS might impair the appearance, increase permeability thereby reducing its durability.

A high possibility of the formation of efflorescence is possible when activators that are less soluble such as sodium sulphate are used, or when moist curing is followed by a dry curing. Curing AAS samples at relative humidity higher than 95% might be effective in preventing or reducing the amount of efflorescence formed. Higher curing relative humidity would prevent the evaporation of the water with free alkali, resulting in insufficient free alkali to react with the carbon dioxide in the air. However, this is not practicable in cast in-situ AAS concrete where the exposure conditions cannot be fully controlled. In addition, efflorescence is mostly associated with AAS activated with high concentrations of alkali solutions [90]. Efflorescence due to high concentration of alkali has been attributed to the availability of excess alkali to react with atmospheric carbon dioxide.

3 Review Summary

There are currently numerous findings regarding the durability of AAS composite that are exposed to different aggressive environmental conditions [91–94]. Based on this review, the following assertions are made:

- Limited long-term durability record: despite the existence of AAS for over a century, there exist limited documented data on the long-term durability of AAS. These limitations also contribute to its non-acceptance by relevant stakeholders in the built environment.
- Inadequate test methods: Some of the OPC based standards currently used to test the durability of AAS has been found to be inadequate. This is as a result of the different

reaction process and products of AAS. An example is the carbonation test, which has been found to be non-representative of the carbonation occurring in AAS.

- Studies attest to the fact that AAS has good resistance to ASR, however, there is no convincing proof of this, as there is no full understanding of how this happens, and the extent or amount of alkali bounded to hydration products.

4 Conclusions

This study focuses on a mini review of the durability properties of alkali-activated slag composite, and the following conclusions were drawn:

- Owing to the variance in the view of researchers, further investigations are necessary to ascertain factors that alter permeability of AAS composite. Different admixtures or micro filling nano materials may be dosed with the AAS mixture to possibly enhance its pore structures.
- Studies have shown that slag enhances the pore structures of AAS composite, by the activity of the hydration products. However, the mechanism of the slag application is still ill defined. Therefore, a more detailed experimental design and optimization of the slag content required for AAS matrix development is required.
- Higher strength loss in OPC exposed to sulphate attack is attributable to the formation of magnesium silicate hydrate (M-S-H) and gypsum because of interaction between the magnesium ions and calcium silicate hydrate (C-S-H).
- It is suggested that a further assessment of sulphate attack on AAS composite when it is altered with mineral admixtures is required. Obviously, mineral admixtures are bound to influence the hydration phenomenon and pore structures.

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