

Alkali-silica reaction resistance versus susceptibility of geopolymers binders

Stephen Ekolu^{1,*}, Léonel Tchadjié¹ and Abdolhossein Naghizadeh²

^{1,*} Department of Civil Engineering, Nelson Mandela University, South Africa

² Department of Engineering Sciences, University of the Free State, South Africa

Abstract. Alkali-silica reaction (ASR) is a deterioration chemical process that causes expansion along with cracking of cement paste and aggregate particles, resulting in concrete degradation. Numerous factors influence ASR including aggregate reactivity, cement alkali content and moisture availability. Due to the high alkali content of the activator, the risk of ASR could be anticipated to be greater in geopolymers than in Portland cement concrete. This article reviewed the susceptibility or resistance of geopolymers to ASR deterioration, based on published data in the literature. Generally, the vulnerability of geopolymers to ASR expansion is influenced by two factors comprising, the chemical composition of the aluminosilicate precursor and the alkaline activator solution characteristics. It is evident that low-calcium geopolymers exhibit very much lower ASR expansion than high-calcium geopolymers. Moreover, ASR expansion increases with increase in the alkali (M_2O with $M = Na, K$) concentration of the geopolymers and declines as the silicate modulus rises SiO_2/M_2O . Calcium-rich geopolymers have a higher risk that may exhibit ASR attack, owing to the formation of the more expansive sodium-calcium-ASR gel.

1 Introduction

Geopolymer binders are formed when aluminosilicate minerals react with an activator solution, often potassium or sodium silicate [1]. Aluminosilicate materials and industrial by-products including fly ash, ground granulated blast-furnace slag (GGBS), volcanic ash and metakaolin etc., are often used to synthesize geopolymers due to their high silica and alumina content [2-4]. When designed appropriately, geopolymers reduce the cement industry's high CO_2 footprint by 80 % less CO_2 than Portland cement [5].

Geopolymer binder systems, in general, display a variety of superior properties that make them suitable for specific applications including rapid hardening, high early strength, chemical resistance, high-temperature resistance and low permeability [2,6]. However, the long-term and durability properties of geopolymers are still not fully understood, particularly in large-scale applications [7-9]. For instance, reservations might be expressed about the alkali-silica reaction (ASR) behaviour of geopolymers since their production requires a strong alkaline activator [7].

ASR is a detrimental chemical reaction that occurs in the Portland cementitious system and manifests itself through changes in the pore structure [10,11], by causing cracking of both the cement paste and of the aggregates, resulting in deterioration of concrete microstructure [10,11]. It usually takes many years for ASR to develop to an extent where significant damage is visible on the

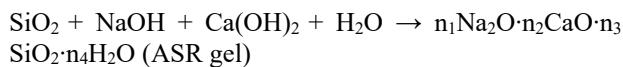
concrete surface [11]. The rate of reaction and the associated deterioration and cracking depends mainly on three factors comprising the reactivity of aggregate, alkali levels in the cement and availability of moisture [11,12]. Due to high alkali concentration of the activator, the potential risk of ASR would be expectedly greater in geopolymers than in Portland cement concrete, but in contrast, it is the reverse. However, ASR behaviour of geopolymers is not fully understood. The objective of this article is to review the ASR behaviour of geopolymers and determine factors responsible for resistance or susceptibility responses of the binder system.

2 Alkali-silica reaction

ASR is the most common type of alkali-aggregate reaction (AAR) [10]. The other type of AAR is alkali-carbonate reaction (ACR), which is less prevalent than ASR and may occur between alkali from the cement paste and dolomite particles [13]. ASR occurs when reactive non-crystalline silica found in various aggregates, reacts with the alkalis (Na^+ or K^+) from cement paste, in the presence of sufficient moisture [10]. This leads to formation of a reaction product referred to as silica gel, which accumulates on surfaces of aggregate particles. As the gel imbibes moisture, it expands in volume over time, resulting in stresses inside the concrete. Once expansion of the silica gel can no longer be accommodated in the pore structure, concrete then cracks in tension [10,12].

* Corresponding author: stephen.ekolu@mandela.ac.za

The ASR mechanism is divided into three stages, which may be summarized using the following equation [14].



The produced gel has an expansive tendency in the reaction described above, depending on the calcium oxide (CaO) content [14]. It is worth noting that ASR may occur only upon fulfillment of the following three criteria, i.e. if:- the aggregates have enough amorphous silica, the cement paste contains enough alkali, and sufficient water is available to drive the reaction. Ordinary Portland cement (OPC) is typically considered to be non-expansive, if it contains no more than 0.6 wt% of the alkali equivalent (Na_2Oeq) [15].

3 Factors affecting alkali-silica reaction in geopolymmer binders

Research literature on ASR behaviour of geopolymers binders, is relatively limited. Most research monitors ASR expansion in geopolymers binders based on the accelerated mortar bar test (AMBT) described in ASTM C1260 (2021). It may be noted that the AMBT was developed for ASR testing of Portland cement. AMBT is a very rapid test that involves soaking of mortar samples in 1 M NaOH solution at 80°C for 14 days. If the expansion is less than 0.1% at 14 days, the aggregate is innocuous, but if expansion exceeds 0.1%, the aggregate is considered to be reactive [16]. Under similar conditions of testing, geopolymers binders are more resistant to ASR than OPC, despite the very high alkali content of the former. Generally, the vulnerability of geopolymers binders to ASR is influenced by two factors comprising the composition of the activator solution and the type of aluminosilicate raw material [7,15].

3.1 Effect of aluminosilicate raw materials

Several natural aluminosilicate materials and industrial by-products including metakaolin, bauxite, fly ash, volcanic ash, slag, etc., have been explored as raw materials for geopolymers. Depending on chemical compositions of these materials, they yield geopolymers binders that can be classified into two categories of low-calcium and high-calcium geopolymers systems. It is well-known that calcium may significantly affect the ASR expansion of cement-based materials that contain reactive aggregates [7,11].

3.1.1 Low-calcium geopolymers systems

This type of binder arises from use of raw materials such as metakaolin, Class F fly ash, bauxite, volcanic ash etc. that contain a relatively high amount of aluminium. Most studies on ASR in low-calcium geopolymers binder systems, have been done using Class F fly ash as the aluminosilicate precursor. Lei et al. [9] investigated the pore solution composition in low-calcium fly ash-based geopolymers concrete for one year. The ASR expansion of

specimens was monitored using the concrete prism test (CPT) according to ASTM C1293 [17]. Type I Portland cement containing Na_2Oeq of 0.66 wt%, was used for the OPC specimens. As shown in Figure 1, the OPC concrete prisms expanded rapidly over the first two months before slowing down. In 9 months, the average OPC prism expansion exceeded the one-year recognised limit of 0.04%. In comparison, the fly ash geopolymers exhibited almost no indication of expansion, giving merely 0.006% after 12 months. Evidently, the ASR resistance of fly ash-based geopolymers concrete, was superior compared to that of OPC concrete. It was reported that geopolymers expanded less due to reduced alkalinity of the pore solution. Indeed, early in the geopolymers process, fly ash dissolution consumes hydroxyl ions, decreasing the pH of the pore solution from 13.8 to 12.6 in just one day. Additionally, calcium deficiency and aluminium availability in the geopolymers pore solution, enhances ASR resistance of geopolymers concrete.

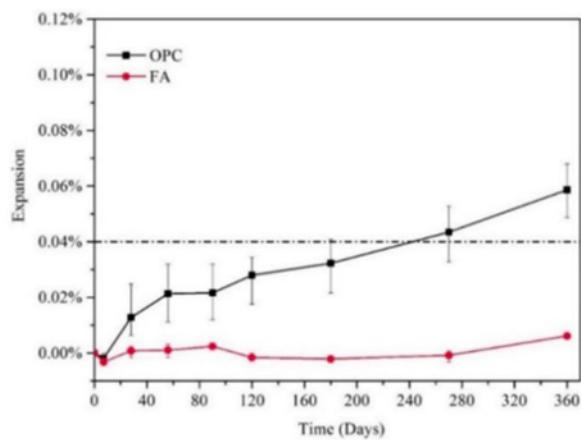


Figure 1 Expansion results of ordinary Portland cement (OPC) and fly ash geopolymers concrete prisms [9].

Pouhet and Cyr [18] studied the behaviour of metakaolin-based geopolymers in the presence of alkali-reactive aggregates. Geopolymers mortars were prepared using metakaolin, sodium waterglass activator solution and six different aggregate types of varied ASR reactivity levels. CEM I 52.5 N was used to prepare OPC mortar as the control mixture. Sodium silicate with a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of 1.68 was used as an alkaline activator solution for geopolymers synthesis. The samples were cured at 60°C and 95% relative humidity (RH) for ages of up to 250 days. They found that despite the presence of high alkali levels in geopolymers mixtures, the latter showed no swelling or significant loss of stiffness, and it outperformed OPC in terms of ASR resistance. The high ASR resistance of metakaolin-based geopolymers, was explained by the rapid drop in pH inside the pores of hardened geopolymers mortars, from about pH = 12 after 14 days to pH = 10.5 after 6 months. This low pH in hardened geopolymers mortar, considerably prevented alkali reaction with reactive aggregates. Additionally, the metakaolin's low CaO content of 2 wt%, also contributed to the binder's low ASR susceptibility.

In general, most research has found that the risk of ASR is extremely low in low-calcium geopolymers systems, which may be attributed to three major causes [7,19–21] comprising the low alkalinity of the hardened geopolymer concrete, calcium insufficiency, and aluminium availability in the geopolymer pore solution.

3.1.2 High-calcium geopolymers systems

The rapid strength development of high-calcium geopolymers at room temperature is a key driver of the extensive worldwide research on geopolymers binders. Raw materials such as Class C fly ash and slag are used to produce this type of binder system. Mixtures made by combining low-calcium aluminosilicate with calcium-rich materials, are likewise included in this category. It is well-established that GGBS effectively mitigates ASR in Portland cement mixtures [7,14]. While high-calcium geopolymers containing GGBS or Class C fly are more prone to ASR, their expansion values are typically below those of OPC system [12,14,15,17]. Tänzer et al. [15] found that the high inherent alkali content of slag-based geopolymers increased the risk of ASR. Similarly, Fernandez-Jimenez and Puertas [14] investigated the expansion of GGBS-based geopolymers mortars. The alkali activator used was NaOH solution containing 4 wt% Na₂Oeq. The AMBT was employed in accordance with ASTM C1260 [16], and results were compared to those of mortars prepared using CEM I 42.5. Findings confirmed that GGBS-based geopolymers mortars exhibited ASR expansion, but at a slower rate than OPC mortars. The ASR expansion of GGBS-based geopolymers mortars, was caused by the formation of sodium and calcium-silicate-hydrate reaction products.

Mahanama et al. [22] examined the influence of GGBS content on ASR expansion in fly ash based geopolymers mortars. The AMBT was used to determine the expansion characteristics of mortar bars containing reactive aggregates, as specified in AS 1141.60.1 [23]. Results showed that ASR expansion values of geopolymers mortars, increased with increase in GGBS content. At 10 wt% GGBS content, ASR expansion was close to 0.1 %. But the geopolymers mortars containing 20 wt% and 50 wt% GGBS exhibited higher ASR expansions exceeding the 0.1 % limit [23]. However, the ultimate expansion levels for GGBS geopolymers mortars were delayed and remained lower than that of OPC control mortar, as seen in Figure 2. The observed increase in ASR expansion values with rise in GGBS content, was due to the presence of calcium at the ASR gel formation site, which induced Ca²⁺ incorporation into the main sodium-based ASR gel, resulting in formation of the more expansive sodium-calcium-ASR gel.

The ASR expansion values of high-calcium geopolymers systems are higher than those of low-calcium systems. Also, calcium-rich geopolymers systems may fail the AMBT test, thereby depicting high ASR risk, by exceeding the 0.1% expansion limit at 14 days [22]. However, such binder mixtures still typically expand less than OPC concretes. Generally, the chemistry of these

calcium-rich aluminosilicate materials mainly controls the ASR mechanism.

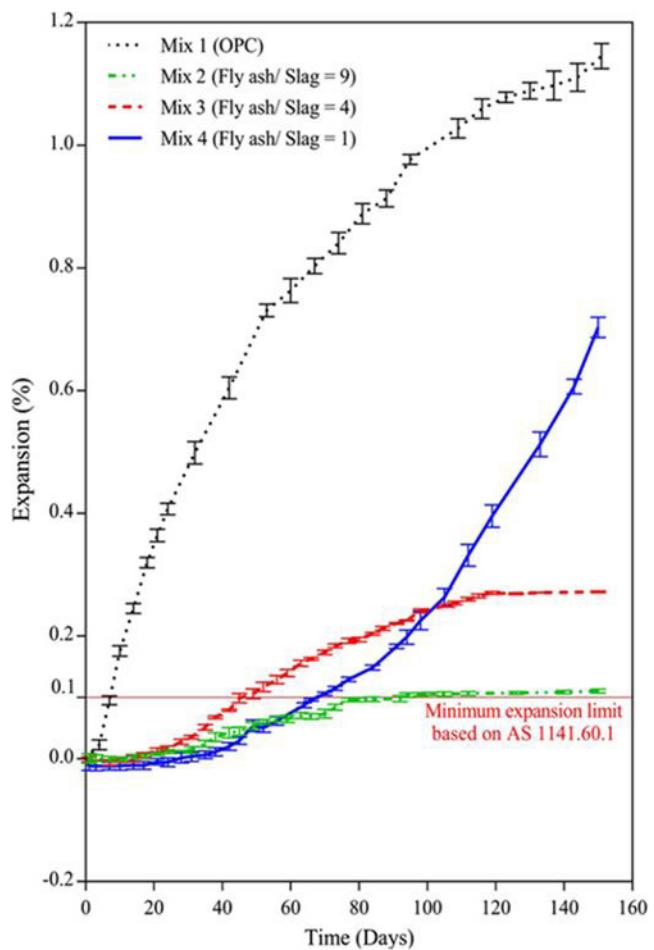


Figure 2 Expansion of ordinary Portland cement (OPC) versus geopolymers fly ash-slag mortar bars [22].

3.2 Effect of activator solution

The most common activator solution for geopolymers synthesis is a combination of sodium (Na)/potassium (K) hydroxide and an Na/K silicate solution [4]. Given the essential role of cation and anion species in the activator solution during geopolymersynthesis, geopolymers can have varied microstructures and consequently give distinct ASR behaviours, depending on the activator type(s) used [24]. Generally, ASR expansion increases with increase in the alkali (M_2O with $M = Na, K$) content of the geopolymers binder mixture, and declines as the silicate modulus SiO_2/M_2O [15,20,25] rises. Naghizadeh and Ekolu [24] investigated the effect of activator solution characteristics and content, on ASR behaviour of fly ash-based geopolymers mortars. Results indicated that the liquid-to-solid (L/S) ratio was the most significant parameter influencing ASR expansion. Increasing L/S and NaOH concentration in the activator promoted ASR expansion of fly ash-based geopolymers mortars. These results agreed with the findings of Williamson and Juenger [8], who also observed that increasing the concentration of alkali activator solution, lowered the

strength of fly ash-based geopolymer concrete, while increasing the potential for ASR expansion.

Indeed, increasing the activator solution concentration above the appropriate quantity necessary for optimal strength development, increases the pore solution alkalinity. Consequently, extra alkali in the pore solution promoted ASR expansion. Tänzer et al.[15] further studied the effects of different silicate moduli of the activator solution, on ASR expansion of slag-based geopolymer mortar. The sodium and potassium silicate solutions used were of different $\text{SiO}_2/\text{M}_2\text{O}$ (with M = Na, K) molar ratios in the range of 0.5-2.0. Borosilicate glass was used as the reactive aggregate. Results showed that a lower silicate modulus of the activator minimizes ASR risk. It was confirmed that the effect of alkali concentration on expansion behaviour was also dependent on the silicate modulus and cations (Na^+ or K^+) of water glass. However, it was reported that potassium silicate solution with a $\text{SiO}_2/\text{K}_2\text{O}$ molar ratio of 1.0 had an adverse impact of increasing ASR expansion. The observed increase in ASR expansion was attributed to the presence of potassium-containing silica gel, which absorbs higher quantities of water than sodium-containing silica gel. The activator solution with $\text{SiO}_2/\text{K}_2\text{O}$ of 0.75 was recommended to be suitable for producing a geopolymer binder of low ASR expansion and good strength development.

4 Conclusions

Despite their high alkali content, geopolymer binders are insignificantly or are much less likely to be affected by ASR attack than ordinary Portland cement. Generally, the susceptibility of geopolymer binders to ASR expansion is influenced by two factors comprising, the chemical composition of the aluminosilicate precursor and the alkaline activator solution characteristics. Low-calcium geopolymer binder systems typically exhibit very low ASR expansion compared to high-calcium geopolymer binders. The high ASR resistance of low-calcium geopolymer binders, is explained by the low alkalinity of the final hardened geopolymer matrix, calcium insufficiency, and aluminium availability in the geopolymer pore solution. Moreover, ASR expansion usually increases with rise in alkali (M_2O with M = Na, K) content of the geopolymer binder mixture and declines as the silicate modulus rises ($\text{SiO}_2/\text{M}_2\text{O}$). Calcium-rich geopolymer binders have a higher risk that may or may not exhibit ASR attack, depending on the type of aluminosilicate raw material, among other factors. In such calcium-rich geopolymer binders, Ca^{2+} ions become incorporated into the sodium-based gel, in turn forming the more expansive sodium-calcium-ASR gel.

References

- [1] Tchadjie L.N. and Ekolu S.O (2018), Enhancing the reactivity of aluminosilicate materials toward geopolymer synthesis, *Journal of Materials Science* 53, 4709–4733. <https://doi.org/10.1007/s10853-017-1907-7>.
- [2] Naghizadeh A. and Ekolu S.O. (2019), Method for comprehensive mix design of fly ash geopolymer mortars, *Construction and Building Materials* 202, 704–717.
- [3] Naghizadeh A. and Ekolu S.O. (2017), Pozzolanic materials and waste products for formulation of geopolymer cements in developing countries: a Review, *Concrete Beton, Jour. Concrete Society of Southern Africa*, Nov 2017, Number 151, 22-31.
- [4] Ekolu S.O., Thomas M.D.A and Hooton R.D. (2006), Studies on Ugandan volcanic ash and tuff, Proc. 1st Intl. Conf. on *Advances in Engineering and Technology*, Entebbe, Uganda, July 75-83.
- [5] Davidovits J. (2011), Geopolymer Chemistry and Applications, 3rd Ed., *Institut Géopolymère*, France,.
- [6] Liew Y.M., Heah C.Y., Mustafa A.B., Kamarudin H. (2016), Structure and properties of clay-based geopolymer cements: A review, *Progress in Materials Science* 83 595–629.
- [7] Cyr M. and Pouhet R. (2015), Resistance to alkali-aggregate reaction (AAR) of alkali-activated cement-based binders, *Woodhead Publishing Limited*. <https://doi.org/10.1533/9781782422884.3.397>.
- [8] Williamson T. and Juenger M.C.G. (2016), The role of activating solution concentration on alkali-silica reaction in alkali-activated fly ash concrete, *Cement and Concrete Research* 83, 124–130.
- [9] Lei J., Fu J. and Yang E. (2020), Alkali-Silica Reaction Resistance and Pore Solution Composition of Low-Calcium Fly Ash-Based Geopolymer Concrete, *Infrastructures* 5, 2–15.
- [10] Stanton T.E. (1942), Expansion of concrete through reaction between cement and aggregate, *Transactions of American Society of Civil Engineers* 107, 54–84.
- [11] Saha A.K., Khan M.N.N., Sarker P.K. Shaikh F.A. and Pramanik A. (2018), The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review, *Construction and Building Materials* 171, 743–758.
- [12] Salim M.U. and Mosaberpanah M.A. (2021), The mechanism of alkali-aggregate reaction in concrete/mortar and its mitigation by using geopolymer materials and mineral admixtures: a comprehensive review, *European Journal of Environmental and Civil Engineering* 0, 1–41. DOI: 10.1080/19648189.2021.1960899
- [13] Sanchez L.F.M., Fournier B., Jolin M., Mitchell D., and Bastien J. (2017), Overall assessment of Alkali-Aggregate Reaction (AAR) in concretes presenting different strengths and incorporating a wide range of reactive aggregate types and natures, *Cement and Concrete Research* 93, 17–31.

- [14] Fernandez-Jimenez A. and Puertas F. (2002), The alkali-silica reaction in alkali-activated granulated slag mortars with reactive aggregate, *Cement and Concrete Composites* 32, 1019–1024.
- [15] Tänzer R., Jin Y. and Stephan D. (2017), Effect of the inherent alkalis of alkali-activated slag on the risk of alkali-silica reaction, *Cement and Concrete Research* 98, 82–90.
- [16] ASTM C1260 (2021), Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method), *American Society for Testing and Materials*, 1–5. <https://doi.org/10.1520/C1260-21.2>.
- [17] ASTM C1293 (2020), Standard test method for determination of length change of concrete due to alkali-silica reaction, *American Society for Testing and Materials* 1–7. <https://doi.org/10.1520/C1293-20A.2>.
- [18] Pouhet R and Cyr M. (2015), Alkali – silica reaction in metakaolin-based geopolymer mortar, *Materials and Structures*, 48 571–583.
- [19] Razak S.N. and Nuruddin M.F. (2014), The effects of alkali-silica reaction (ASR) towards fly ash-based geopolymer concrete, *Applied Mechanics and Materials* 699, 271–276.
- [20] Yang M., Paudel S.R. and Asa E. (2020), Comparison of pore structure in alkali-activated fly ash geopolymer and ordinary concrete due to alkali-silica reaction using micro-computed tomography, *Construction and Building Materials* 236 1–11.
- [21] Naghizadeh A. and Ekolu S.O. (2022), Activator-related effects of sodium hydroxide storage solution in standard testing of fly ash geopolymer mortars for alkali-silica reaction, *Materials and Structures* 55, 1–16. <https://doi.org/10.1617/s11527-021-01875-8>.
- [22] Mahanama D., de Silva P., Kim T., Castel A., Khan M.S.H. (2019), Evaluating effect of GGBFS in alkali-silica reaction in geopolymer mortar with accelerated mortar bar test, *Journal of Materials in Civil Engineering* 31 04019167.
- [23] AS 1141.60.1 (2014), Methods for sampling and testing aggregates Part 60.1: Alkali aggregate reactivity—Accelerated mortar bar method, *Standards Australia* 1–17.
- [24] Naghizadeh A. and Ekolu S.O. (2017), Investigation of mixture factors influencing alkali-silica reaction in fly ash-based geopolymer mortars, in: *Int. Conf. on Advances in Construction Materials and Systems*, (ICACMS-2017), Chennai, pp. 395–400.
- [25] Al-otaibi S. (2008), Durability of concrete incorporating GGBS activated by water-glass, *Construction and Building Materials* 22, 2059–2067. <https://doi.org/10.1016/j.conbuildmat.2007.07.023>.