

ALKALI ACTIVATED MATERIALS: REVIEW OF CURRENT PROBLEMS AND POSSIBLE SOLUTIONS

Adeyemi Adesina ⁽¹⁾

(1) Concordia University, Montreal, Canada

Abstract

Focus on alkali-activated materials (AAMs) have increased in recent years due to its possibility to be a substitute for the ordinary Portland cement (OPC). However, the development of AAM that would be a viable substitute for OPC is still impeded due to several problems faced during its production, and properties of the resulting AAMs. Finding a substitute for OPC is imminent as a result of its contribution of about 7% to the world's human-induced carbon dioxide emission. The amount of emission is expected to increase in the coming years due to increase in development all over the world. Therefore, it is necessary to develop alternative green binder that would contribute less emission to the environment while conserving natural resources deposit.

This review explored the current problems hindering the universal acceptance and large-scale application of AAMs. It was concluded that with more research and development on user-friendly activators with low embodied energy and carbon, AAMs will be able to compete as a viable substitute for OPC.

1. Introduction

Alkali-activated materials (AAMs) have gained huge attention recently in the concrete industry due to its viability to be used as a replacement for the conventional ordinary Portland cement (OPC). AAMs are obtained by activating an aluminosilicate precursor with an alkaline activator. The need for replacement of OPC in concrete is imminent due to its high embodied carbon and energy [1]. Approximately 1 tonne of carbon dioxide is emitted with an equivalent amount of OPC produced [2]. The carbon dioxide emission is from the calcination of raw materials and high amount of energy used during OPC's production. As OPC is the main binder in concrete, and billions of tonnes of concrete produced annually; OPC's production contributes between 5 – 10% of the total world anthropogenic greenhouse gases emission [3].

Higher strength and durability properties of AAMs compared to OPC concrete has made it attract huge research from the concrete industry. And majorly, AAMs has shown the possibility of having a huge reduction in carbon dioxide emissions between 55 – 75% of conventional OPC concrete [4]. In addition, AAMs conserves the natural deposits of raw materials such as

limestone, as the aluminosilicate materials used for AAMs are by-products of other industrial processes. However, this green advantage is posed with several limitations. Some of the major limitations are quick setting times and high drying shrinkage. These limitations have inhibited the universal acceptance and commercial use of AAMs. Depending on the aluminosilicate materials used, AAMs can be further divided. For example, alkali-activated slag (AAS) is a type of AAMs which uses slag as the aluminosilicate precursor. As the component in AAMs is different from that of OPC, its chemical composition and process differ also [5, 6].

This review is aimed at exploring the major limitations of AAMs, and possible solutions for the limitations. It is anticipated that this review will be a great reference for researchers, construction managers and engineers in the field of construction in general.

2. Current AAMs problems

The problems currently faced by AAMs are evident in the fresh and hardened properties of AAM. Some of the fresh properties limitations are short set times and extremely low flowability. While some of the hardened properties limitations are high drying shrinkage and low volume stability. Some of the major limitations are further explained as follows;

2.1 Short setting time

Two major factors have been identified to affect the setting time of AAMs. These factors are the type of activator and the activator content [7]. Short setting time in AAMs is observed when sodium silicate is used as an activator. Earlier studies [8, 9] reported flash setting of AAMs when activated with sodium silicate. However, the quick setting of AAMs is more pronounced in those activated with sodium silicate compared to sodium hydroxide. The setting times of AAMs activated with a combination of sodium silicate and sodium hydroxide is longer than when activated with only sodium silicate [10]. Short set time caused by sodium silicate activation has been attributed to the initial formation of calcium silicate hydrate. Whereas, the extended setting time observed in AAS activated with sodium hydroxide and sodium carbonate is as a result of the formation of polysilicates hydrates and calcium carbonate respectively [11, 12]. Increase in the ambient temperature has been recorded to shorten the setting time of AAS [4]. However, no significant effect was found on the setting time of AAS when sodium silicate and sodium hydroxide was used to activate AAS. The difference in the effect of ambient temperature on the setting time of different AAS activated with various activator has been attributed to the difference in the chemical composition of the activator [4].

2.2 Elevated curing temperature

AAMs with low calcium aluminosilicate precursors such as class F Fly ash fly ash requires an elevated temperature to accelerate the dissolution of the monomers. In order to achieve a similar strength of AAM made with fly ash compared to that of OPC, an elevated temperature between 60 to 80°C is required [7, 13]. Though the elevated temperature is not required for high calcium aluminosilicate precursors such as slag. However, it has been reported that curing AAMs made with slag reduces the high drying shrinkage associated with it [10]. This elevated temperature requirement has limited the practical large-scale application of AAMs for different applications. However, elevated curing is reasonable in applications such as precast concrete, where the concrete is made in the plants, and it is easier to control the variables during production. Use of elevated temperature curing however consumed huge amount of energy and

release more carbon dioxide to the environment thereby increasing the overall embodied energy and carbon of AAMs.

2.3 High drying shrinkage

Shrinkage in AAMs has been found to be higher than that of OPC, especially those with slag as aluminosilicate precursors, and activated with sodium silicate [14, 15]. Formation of gel that is rich in silica has been attributed to the high shrinkage in slag activated with sodium silicate [16, 17]. As the rich silica gel loses moisture during drying, it causes microcracks within the AAS paste. Also, higher shrinkage in AAMs has been attributed to its high quantity of mesopores compared to that of OPC [18].

2.4 Non-user friendly activator

Based on open literature, sodium silicate and sodium hydroxide are the most used activators for AAMs [1-5]. These common activators are expensive, corrosive and the highest contributor of embodied energy and carbon to AAMs. The high cost associated with AAMs activated with these activators have discouraged contractors in embracing this sustainable material. In addition, the high embodied energy and carbon of some of the common activators (i.e. sodium silicate and sodium hydroxide) have eliminated the advantage of using AAMs as a sustainable building material. Also, the corrosiveness of these activators will prevent its large-scale transportation and application as special handling will be required.

2.5 Unknown long-term durability and performance

Most durability properties of concrete are associated with its permeability, which can be measured through its water absorption. Generally, AAMs has been reported in most studies to be more resistant to several detrimental forces in the environment that affects its durability. However, to date, there's no consensus on the water absorption of AAMs due to limited data availability and variation in the available data. For example, Bernal et al [19] and Yang et al [20] concluded that the water absorption of slag activated with sodium silicate is higher than that of OPC. However, some other studies [21, 22] recorded a contradicting observation in which the water permeability was lower than that of OPC. Albitar et al [23] also reported a lower water absorption for AAMs. These contrasting results and lack of extensive long-term results have discouraged project managers and contractors to embrace this innovative sustainable material (i.e. AAMs). Another durability aspect that there's no consensus yet is the alkali-aggregate reaction (AAR). Though the aluminosilicate precursors used for AAMs are used to curb AAR in conventional concrete, contradicting results exists in the open literature. Several studies reported lower AAR expansion in AAM when reactive aggregates are used. However, Bakharev et al. [24] reported that higher expansion when reactive aggregates were used. It should be noted that AAMs usually contain higher amount alkali due to activator used, therefore the probability of AAR to occur is higher. There exist specifications to limit the equivalent sodium oxide in OPC to 0.8% to prevent the occurrence of AAR, however, AAMs contain a higher amount of sodium oxide equivalent. Resistance to AAR in AAMs reported in some studies might be as a result of the high alkali present in AAMs been bounded to the hydration products formed, thereby reducing the overall alkalinity in the pore solution [25, 26]. However, the practical proof exists of the quantity of alkali bounded to formed products [27].

2.6 Supply market for raw materials

Compared to limestone which is the main raw material for OPC, the aluminosilicate materials use of AAMs are not readily available everywhere, and the type available varies from different geological location. For examples, rice husk ash is readily available in India, whereas its production is limited in Canada, and slag and fly ash is more readily available. This variation in large quantity availability limits the universal use of AAMs compared to that of OPC.

2.7 Lack of universal specification and standard for AAMs

Most construction and research involving AAMs currently use the specifications and standards available for OPC, and OPC concrete. However, it has been found that some of these standards/ tests give false results as the chemistry of AAMs are different from that of OPC. Byfors et al [28], Bakharev [10], and Deja [29] observed that the carbonation rate of alkali-activated slag (AAS) concrete is faster than that of OPC using accelerated carbonation test. However, it concluded that this accelerated test used for OPC is not suitable for AAMs as it overestimates the carbonation of AAMs [30, 31].

2.8 Efflorescence

Efflorescence is the whitish product that is formed on the surface of the concrete. The formation of this whitish products in AAMs has been associated with the use of high concentration of sodium hydroxide as an activator for AAMs [58]. The whitish product is bicarbonate crystals formed as a result of the reaction of alkali that leached with the carbon dioxide in the environment. Ideally, low amount of bicarbonate formation on the surface of AAMs does not pose any danger to its durability and mechanical properties [58]. But the high formation of this whitish product might be detrimental to the hardened properties of the AAM. Also, high amount of bicarbonate crystals on the surface of AAM would affect its aesthetics. Use of sodium sulphate as activator might also lead to the formation of alkali sulphates on the surface of AAMs. This formation of alkali sulphate is as a result of the low solubility of sodium sulphate [32].

3. Possible solutions to AAMs problems

Use of retarding admixtures employed for OPC concrete can be used to extend the setting time of AAS as there exists currently retarding admixtures made specifically for AAMs. As using sodium silicate is mainly responsible for most quick set times in AAMs, use of alternative activators such as sodium carbonate which produces similar set times similar to that of OPC will be a viable option. Shrinkage in AAMs can be controlled by the use of alternative activators instead of the conventional sodium silicate. For example, the use of sodium carbonate to activate slag has been found to reduce the shrinkage of AAS to give shrinkage similar to that of OPC [14]. Other possible ways to reduce the shrinkage in AAMs includes the use of shrinkage reducing admixtures (SRAs) [33, 34], internal curing [33], heat curing [16, 35]. Use of supplementary cementitious materials (SCMs) [35, 36] can also reduce the shrinkage of AAMs. Also, air entrainers used for OPC concrete has been found to reduce the shrinkage in AAS [37]. Use of OPC by 10% by mass of the aluminosilicate material used has also been reported to reduce the shrinkage of AAMs [38]. Also, moist curing of AAMs has been found to reduce shrinkage significantly as it prevents rapid loss of moisture from the AAM matrix

[18]. Other shrinkage mitigation techniques include fibre reinforcement [39], use of lightweight aggregates, high aggregate content, etc.

Proper moist curing and use of activators with lower concentrations would prevent the formation of high amount of bicarbonate crystals (i.e. efflorescence) on the surface of AAM concrete. Curing of AAMs at relative humidity higher than 95% has been found to prevent the formation of efflorescence [32].

4 Conclusions

This review showed that AAMs is a good substitute for OPC if all its limitations can be overcome. Based on this review, the following conclusions can be drawn;

- Use of alternative green activators will go a long way in eliminating most of the challenges faced by the fresh and hardened properties of AAMs
- Shrinkage in AAMs can be controlled with proper moist curing, use of shrinkage reducing admixture, and good mix design which employs the use of high coarse aggregate content
- Involvement of different stakeholders in the concrete industry will propel more acceptance of AAMs as an alternative sustainable building material.

References

- [1] Flower, D., and Sanjayan, J. Greenhouse gas emissions due to concrete manufacture," 26 International Journal of Life Cycle Assessment, (2007) 282- 288
- [2] Cabeza, F et al, Low carbon and low embodied energy materials in buildings: a review Renew. Sustain. Energy Rev., 23 (2013), 536-542
- [3] Scrivener, K.L and Kirkpatrick, R. J., Innovation in use and research on cementitious material Cem. Concr. Res., 38 (2008)128-136
- [4] Zivicz, V., Effects of type and dosage of alkaline activator and temperature on the properties of alkali-activated slag mixtures Construction and Building Materials Volume 21, Issue 7, July 2007, 1463-1469
- [5] Pacheco-Torgal, F., et al Alkali-activated binders: A review: Part 1 Historical background, terminology, reaction mechanisms and hydration products Constr. Build. Mater.(2008), 1305-1314
- [6] Zhang, et al. Compositional, microstructural and mechanical properties of ambient condition cured alkali-activated cement Constr. Build. Mater., 113 (2016), 237-245
- [7] Duxson, P et al. Geopolymer technology: the current state of the art J Mater Sci, 42 (2007), pp. 2917-2933
- [8] Cheng, Q.H., and Shondeep L. S., A study of rheological and mechanical properties of mixed alkali activated slag pastes. Advn Cem Bas Mat (1994), 178–84.
- [9] Gifford P. M., and Gillot, J. E., ASR and alkali carbonate reaction in activated blast furnace cement concrete. Cem Concr Res (1996) 21–6.
- [10] Bakharev, T. Resistance of alkali-activated slag concrete to carbonation Cem. Concr. Res., (2001),1277-1283
- [11] Hong S. Y. et al. Studies on the hydration of alkali activated slag. In: Proceedings of the third Beijing international symposium on cement and concrete, vol. 2. Beijing; (1993.)1059–1042.
- [12] Brylicky W et al. Alkali activated slag cementitious material for drilling operation. In: Proceedings of the ninth international congress on the chemistry of cement, vol. 3. New Delhi; (1992). 312–318.
- [13] Palomo, A. et al. Alkali-activated fly ashes, a cement for the future Cem Concr Res, 29 (8) (1999), 1323-1329
- [14] Cartwright, C. et al Shrinkage characteristics of alkaliactivated 2slag cements, J. Mater. Civ. Eng. (2014), 401-407

- [15] Ye, H., and Radlinska, A. Shrinkage mechanisms of alkali-activated slag, *Cement and Concrete Research*, (2016), 126-135
- [16] Shi, C. et al *Alkali-activated Cements and Concretes* Taylor and Francis, London and New York (2006)
- [17] Wu, C. Properties and application of alkali-slag cement," *Journal of Chinese Ceramic Society*, (1993). 176-181
- [18] Collins F, Sanjayan J. G. Microcracking and strength development of alkali-activated slag concrete. *Cem Concr Compos* (2001), 345–52.
- [19] Bernal, S. et al Performance of an alkali-activated slag concrete reinforced with steel fibers *Constr. Build. Mater.*, (2010), 208-214.
- [20] Yang, K., et al. Establishment of a preconditioning regime for air permeability and sorptivity of alkali-activated slag concrete *Cem. Concr. Compos.*, 73 (2016), pp. 19-28.

- [21] Mithun, B.M. and Narasimhan, M.C. Performance of alkali activated slag concrete mixes incorporating copper slag as fine aggregate *J. Cleaner Prod.*, (2016), 837-844
- [22] Bernal, S. et al Performance of an alkali-activated slag concrete reinforced with steel fibers *Constr. Build. Mater.*, (2010), 208-214
- [23] Albitar, M. et al Durability evaluation of geopolymer and conventional concretes *Constr. Build. Mater.*, 136 (2017), 374-385
- [24] Bakharev T. et al Resistance of alkali-activated slag concrete to alkali-aggregate reaction. *Cem Concr Res* (2001), 331–4
- [25] Krivenko, P. Sodium sulphate based slag alkaline cements, *Proceedings of 3rd Beijing International Symposium on Cement and Concrete*, Beijing, (1993). 1032-1037
- [26] Tailing, B., and Brandstetr, J. Present state and future of alkali activated slag concrete, *Proceeding of 3rd International Conference on Fly ash, Silica Fume, Slag and Natural Pozzolanas in Concrete*, Trondheim, (1989) 1519-1546.
- [27] Mesto, J. Alkali reaction of alkali activated Finish blast furnace slag, *Silicon Industry*, (1982), 123 -127.
- [28] Byfors, K. et al Durability of concrete made with alkali-activated slag, *Third International Conference Proceedings. Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete* (1989), 1429–1466.
- [29] Deja, J. Carbonation aspects of alkali activated slag mortars and concretes *Silic Ind.*, (2002), 37-42.
- [30] Bernal, S. A et al. Accelerated carbonation testing of alkali-activated slag/metakaolin blended concretes: effect of exposure conditions *Mater. Struct.*, (2014), 653-669
- [31] Bernal, S.A. et al. Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation *Cem. Concr. Res.*, (2013), 127-144.
- [32] Wang S. D, et al Factors affecting the strength of alkali-activated slag. *Cem Concr Res* (1994), 1033–43.
- [33] Saliba J. et al. Influence of shrinkage-reducing admixtures on plastic and long-term shrinkage. *Cem. Concr. Compos.* (2011), 209–217.
- [34] Rajabipour F. et al Interactions between shrinkage reducing admixtures (sra) and cement paste's pore solution. *Cem. Concr. Res.* (2008), 38:606–615.
- [35] Aydin S., and Baradan B. Mechanical and microstructural properties of heat cured alkali-activated slag mortars. *Mater. Des.* (2012), 374–383.
- [36] Rajabipour F. et al Interactions between shrinkage reducing admixtures (sra) and cement paste's pore solution. *Cem. Concr. Res.* (2008), 38:606–615.
- [37] Bakharev et al. Effect of admixtures on properties of alkali-activated slag concrete. *Cem Concr Res* (2000) 367–74.
- [38] Fu-seng W et al Study on modification of the high-strength slag cement material. *Cem Concr Res* (2005), 1344–8.
- [39] Mangat, P.S., and Bordeian, S. Shrinkage of fibre reinforced alkali activated composites. *Cem. Concr. Compos.*, in press