

## **EFFECT OF GREEN ACTIVATORS ON THE PROPERTIES OF ALKALI ACTIVATED MATERIALS: A REVIEW**

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### **Abstract**

The most common types of activators used for alkali-activated materials (AAMs) are sodium hydroxide and sodium silicate. These activators have been found to be corrosive, viscous, expensive, and with high embodied energy and carbon. In addition, the properties of these activators have made the large-scale applications of AAMs possible as a result of the special handling and side effects it has on the properties of the resulting AAM.

Therefore, this review explored the use of alternative green activator used for AAMs and the effects it has on its properties. A green activator herein is classified as an activator that has a less embodied energy and carbon compared to sodium silicate and sodium hydroxide. This study shows the possibility of producing a greener AAM with enhanced strength and durability properties. In addition, it was observed that there's a considerable cost reduction with the use of the green activators compared to the conventional ones.

### **1. Introduction**

The high emission of carbon dioxide due to the production of ordinary Portland cement (OPC) has opened the way for various sustainable initiatives that can be used to reduce these high emissions. These initiatives vary from the partial and total replacement of OPC, to use of alternative fuels and optimization of OPC's production processes. However, the one with the most promising possibility of reducing a significant amount of carbon dioxide is alkali-activated materials (AAMs). Alkali-activated materials create an avenue for 100% replacement of OPC in concrete and use waste materials as one of the major components. AAMs are achieved by alkali activation of aluminosilicate precursors with an alkali source. Examples of aluminosilicate precursor used for AAMs are slag, fly ash, metakaolin, rice husk ash, etc. The alkali activation results in dissolution of aluminate and silicate monomers from the precursor and a gel which hardens is formed. The common types of alkali activators commonly used for AAMs eliminates the sustainable advantage of AAMs over OPC, as they are its major contributor of carbon dioxide.

The most commonly used activators used are sodium silicate and sodium hydroxide. These activators are mostly used due to its resulting high strength. However, these activators produce poor fresh and hardened properties that have limited the universal acceptance and large-scale application of AAMs. The major poor properties ensued from the use of sodium

silicate and sodium hydroxide are quick setting and high drying shrinkage. Quick setting of alkali-activated slag (AAS) which is a type of AAM has been found to result in low workability and flowability of the AAM [12,13]. In addition, these activators are expensive, corrosive, and are the highest contributor of embodied energy in AAM preventing the advantage of using AAM as a binder in concrete [2,5].

As there exists no review in the open literature that focuses on the use of green activators in AAMs, this review explores the use of activators that can be classified as green activators, and the effects they have on the resulting properties of the AAMs. AAMs used herein refers to different types of AAMs which use different types of aluminosilicate precursors. Where significant, the type of AAMs is mentioned. It is anticipated that this review will open a pathway for more application and research on the use of green activators.

## **2. Green activators**

Activators classified as green in this article have a significant lower embodied carbon and energy compared to that of sodium silicate and sodium hydroxide. Also, these green activators are more user-friendly (i.e. less corrosive), and cheaper. Some types of green activators are further explored, alongside with their effect on the properties of the resulting AAMs.

### **2.1 Sodium carbonate**

Compared to sodium silicate and sodium hydroxide, sodium carbonate exists naturally in the environment and can be extracted from sodium carbonate and trona mines [19]. Also, it can be obtained through a chemical procedure (i.e. Solvay) [18]. In addition, it is approximately 3 times cheaper than sodium silicate and sodium hydroxide [9].

However, activating aluminosilicate precursors with sodium carbonate results in lower early age strength compared to those activated with common activators (i.e. sodium silicate and sodium hydroxide). This lower early strength has been attributed to the initial formation of sodium calcium carbonate which delays the activation reaction [4]. Sodium carbonate also results in lower drying shrinkage of AAM compared to those activated with sodium silicate.

AAMs activated with sodium carbonate shows a more practical set time compared to those activated with sodium silicate [4]. The extended set time has been attributed to the initial formation of calcium carbonate, which also results in lower early age strength as mentioned earlier. Also, sodium carbonate lower pH (i.e. 12.6) compared to that of sodium silicate (i.e. 13.4) and sodium hydroxide (i.e. 13.8) is responsible for the extended setting time. Wang et al [22] also attributed the lower early strength of slag activated with sodium carbonate to the activator's lower pH. Slag activated with sodium carbonate has been able to result in higher strength at later ages (i.e. 28 days) which makes it a great alternative for sodium silicate and sodium hydroxide where high early strength is not required [4]. The later higher strength has been attributed to the formation of carbonated compounds which results in a more densified microstructure [4]. Other studies also recorded late higher strength of up to 60MPa at 28 days when sodium carbonate was used to activate slag.

## 2.2 Magnesium oxide

Slag activated by 10 - 20% of magnesium oxide has been found to have a strength about four times that of those activated with calcium hydroxide [16]. However, between 5 – 10% magnesium oxide, the 28 days of the resulting AAM was found to be lower than those activated with calcium hydroxide. Use of magnesium oxide to activate slag has been found to reduce shrinkage and cracking capability of the resulting AAM [16].

Despite the great potential of using magnesium oxide as a green alternative activator for AAMs, it should be noted that the chemical composition of magnesium oxide varies considerably from different locations [1]. Birchall et al. [1] and Mo et al. [11] recorded variations in AAMs properties when different types of magnesium oxide were used. Therefore, proper initial tests should be carried out to determine the optimum proportions for a specific magnesium oxide before a large-scale production is carried out

Though high energy is consumed, and carbon dioxide is emitted during the manufacture of magnesium oxide, the very low amount (i.e. about 10% the mass of the binder) required to activate AAMs still makes the resulting AAM more sustainable compared to OPC [22].

## 2.3 Sodium sulphate

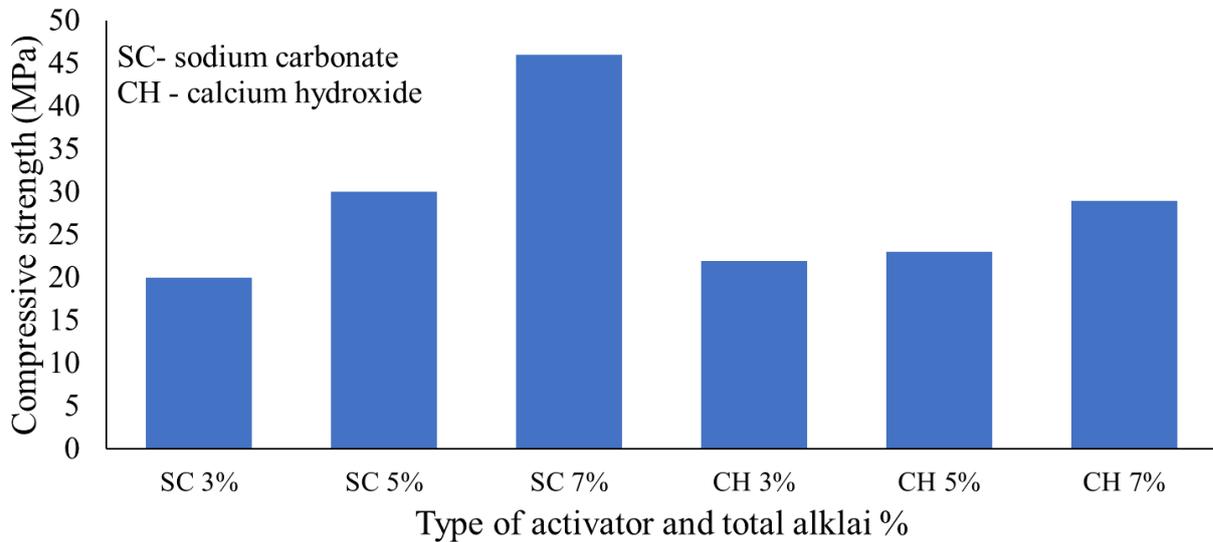
The common activators used for AAMs (i.e. sodium silicate and sodium hydroxide) cannot be mined directly from the environment, therefore they required several industrial processes that are energy intensive and emit a large amount of carbon dioxide into the environment. On the other hand, sodium sulphate can be obtained from natural resources, which eliminates the negative impact production of the common activators have on the environment [14]. Similar to sodium carbonate, AAMs activated with sodium sulphate show low early age strength [23]. This is due to the low alkalinity of the sodium sulphate [14]. Increasing the sodium oxide equivalent of sodium sulphate from 1 to 3% resulted in a significant increase in the early age strength of AAMs [14,15]. However, at 28 days, there's no significant difference between samples activated with 1% and 3% sodium oxide equivalent. Using 1% sodium oxide equivalent to activate slag, Douglas and Brandstetr [3] obtained a 24 hours strength similar to that of OPC

AAMs activated with sodium sulphate exhibited longer setting times compared to those activated with sodium silicate and sodium hydroxide. In addition, AAMs activated with sodium sulphate show excellent workability similar to that of OPC [14], and higher fire resistance [15]. This shows to use sodium sulphate as an activator for large-scale AAMs applications. However, AAMs activated with sodium sulphate exhibited higher drying shrinkage compared to that of OPC, but lower than those activated with sodium hydroxide and sodium silicate [14]. Use of shrinkage reducing admixtures (SRA), OPC, hydrated lime, or fly ash can be used to control the drying shrinkage in AAMs activated with sodium sulphate. A reduction of 43.64% and 58.73% in drying shrinkage was recorded when hydrated lime and OPC was used respectively [14]. Sodium sulphate is also more economical in terms of cost and availability compared to the common activators

## 2.4 Calcium hydroxide

Calcium hydroxide has a lower alkalinity compared to that of sodium silicate, sodium hydroxide, and sodium carbonate. This lower pH has resulted in lower strength gain of AAMs activated with calcium hydroxide due to the slower dissolution of silicate and aluminate monomers from aluminosilicate precursors [8, 24]. When calcium hydroxide is used as AAMs activator, an optimum activator level has to be determined as this type of activators does not

behave like other activators where increasing the concentration leads to higher strength. This is as a result of the low solubility of calcium hydroxide in water, which results in an insignificant change in alkalinity when a higher amount is dissolved in water as observed in **Figure 1** [10]. These results are also similar to Jeonung et al. [7] study where they observed no significant gain in strength when the concentration of the calcium hydroxide was increased



**Figure 1.** 28 days compressive strength of different types of activator and total alkali percentage (data from [10])

Calcium hydroxide is a more user-friendly activator as it safe to handle, less expensive, and readily available for purchase in household stores. Calcium hydroxide is approximately 6 times cheaper than sodium hydroxide [6]. Use of sodium sulphate with calcium hydroxide as AAM activator has been reported to improve the strength of the AAM significantly [17]. The improved strength has been attributed to the formation of ettringite which densifies the microstructure, thereby leading to higher strength [17]. A study carried out by Jeong et al. [7] showed that the early strength of AAMs activated with calcium hydroxide can be improved by the addition of supplementary activators. The supplementary activators used were gypsum, sodium hydroxide, sodium carbonate and sodium sulphate. However, the later age strength was not improved with the addition of supplementary activators. Yang et al [24] used longer curing duration to improve the later age strength of AAM which employs slag as the aluminosilicate precursor. The improved later age strength can be attributed to a more stabilized calcium silicate hydrate

### 3. Conclusions

Based on the short review on the effect of green activators on the properties of AAMs, the following conclusion can be made;

- Use of sodium hydroxide and sodium silicate as activators for AAMs is not a sustainable option, as these common activators cannot be obtained from natural resources, and their production process is energy intensive and emits carbon dioxide to the environment

- In cases where high early strength is not required, activating AAMs with sodium carbonate is a greener alternative, as it results in similar strength at later ages compared to those activated with sodium silicate and sodium hydroxide
- Binary and ternary application of green activators will result in practical early age and later age strength. In addition, the combination of the green activators at right percentages will help to improve the overall durability of AAMs
- More research in the field of green activators is still required as very limited research is available, the majority of all the studies in AAMs employs the use of sodium silicate and sodium hydroxide as activators

## References

- [1] Birchal, V. et al effect of magnesite calcination conditions on magnesia hydration *Miner Eng.* (2000), 1629-1633
- [2] Deventer, J.S.J. et al Chemical research and climate change as drivers in the commercial adoption of alkali-activated materials *Waste Biomass Valoriz.*, (2010), 145-155
- [3] Douglas E, Brandstetr J. A preliminary study on the alkali activation of ground granulated blast-furnace slag. *Cem Concr Res*, (1990), 746–56
- [4] Fernández-Jiménez, A. et al. Alkali-activated slag mortars: mechanical strength behavior *Cem. Concr. Res.*, (1999), 1313-1321
- [5] Habert, G et al. An environmental evaluation of geopolymer based concrete production: reviewing current research trends *J. Clean. Prod.*, (2011), 1229-1238
- [6] ICIS Indicative Chemical Prices A–Z (2015) <http://www.icis.com/chemicals/channel-info-chemicals-a-z>
- [7] Jeong, Y. et al Influence of four additional activators on hydrated-lime [Ca(OH)<sub>2</sub>] activated ground granulated blast-furnace slag *Cement and Concrete Composites* (2016) 1-10
- [8] Kim, M. S. et al Use of CaO as an activator for producing a price-competitive non-cement structural binder using ground granulated blast furnace slag *Cem. Concr. Res.*, (2013), 208-214
- [9] Kostick D. S. Soda Ash: Statistics and Information U.S. Geological Survey (2013)
- [10] Maghsoodloorad, H. et al Recycling phosphorus slag as a precursor for alkali-activated binder; Impact of type and dosage of activator, *Journal Ceramics-Silikáty*, (2014), 227 - 236
- [11] Mo, L et al. Effects of calcination condition on expansion property of MgO-type expansive agent used in cement-based materials *Cem Concr Res*, (2010), 437-446
- [12] Pacheco-Torgal, F. et al Alkali-activated binders: a review. Part 2. About materials and binders manufacture *Constr Build Mater*, (2008), 1315-1322
- [13] Palacios, M and Puertas, F Effect of superplasticizer and shrinkage reducing admixtures on alkali-activated slag pastes and mortars, *Cem. Concr. Res.* (2005), 1358-1367
- [14] Rashad, A. M. Influence of different additives on the properties of sodium sulfate activated slag *Const and Buil Mat*, (2015), 379–389
- [15] Rashad, A. M. et al Chemical and mechanical stability of sodium sulfate activated slag after exposure to elevated temperature. *Cem Concr Res*, (2012), 333–43.

- [16] Shen W. et al Magnesia modification of alkali-activated slag fly ash cement. *J Wuhan Univ Technol Sci Ed*, ( 2011), 121–5.
- [17] Shi, C and Day, R Chemical activation of lime-slag blends V.M. Malhotra (Ed.), *Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete – Proceedings, Fifth International Conference*, vols. 1 and 2, American Concrete Institute, Detroit (1995), pp. 1165-1177
- [18] Shi, C. et al, D. *Alkali-activated Cements and Concretes* Taylor & Francis, Oxon (2006)
- [19] U.S. Geological Survey *Mineral Commodity Summaries: Soda Ash* (2013)
- [20] Wang, J et al Influence of the combination of calcium oxide and sodium carbonate on the hydration reactivity of alkali-activated slag binders. *Journal of Cleaner Production*, (2018), 622-629
- [21] Rashad Alaa M. An exploratory study on sodium sulfate-activated slag blended with Portland cement under the effect of thermal loads. *J Therm Anal Calorim*, (2014), 4345-4347
- [22] Wang S. D, et al Factors affecting the strength of alkali-activated slag. *Cem Concr Res* (1994), 1033–43.
- [23] Xueqan, W. et al. Early activation and properties of slag cement. *Cem Concr Res* (1990), 961–974.
- [24] Yang, K. H. et al Hydration products and strength development of calcium hydroxide-based alkali-activated slag mortars *Constr. Build. Mater.*, (2012), 410-419