



## REVIEW OF MECHANICAL PROPERTIES AND DURABILITY OF ALKALI ACTIVATED SYSTEMS

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**Abstract:** Alkali activated systems are getting popular in construction sector. This increases the demand to understand its performance. An overview of the advances in alkali activated materials (AAMs) produced through activating aluminosilicate raw materials is presented along with a discussion for advantages and disadvantages of this technology. Reaction mechanisms for different aluminosilicate sources with activators were analyzed in order to achieve a good understanding for final products nature, and parameters affecting the process. This was supported with fresh and hardened properties and microstructure analysis. Overall performance including fire resistance, reinforcement bars bond and bond between aggregate and matrix were presented for better understanding of the performance. Moreover, durability performance of AAMs was also discussed in a comparison to cement-based materials.

### 1 INTRODUCTION

The demand for cement has been constantly increasing due to increased infrastructural activities all over the world. Approximately, 15 billion tonnes of concrete are produced annually by concrete industry using about 2 billion tonnes of ordinary Portland cement (OPC) [1]. A lot of concerns regarding carbon dioxide (CO<sub>2</sub>) emission to the atmosphere is being considered as it reached records breaking levels [2]. Portland cement production is one of the major CO<sub>2</sub> contributor sectors. Also as recorded by International Energy Authority, cement industry is responsible for the consumption of about 5% of worldwide industrial energy [3]. In addition, cement production consumes considerable amounts of virgin materials. Therefore, the scientific community is seeking an alternative binder. Recently, alkali activated materials (AAMs) became one of the most important technologies to develop an alternative binder. It is characterized by low CO<sub>2</sub> emission, superior properties including high chemical resistance, outstanding mechanical properties and durability performance compared to that of the OPC. Hence, AAMs are promising alternative binders to OPC.

## 2 OVERVIEW OF ALKALI ACTIVATED SYSTEMS

After lime and OPC, geopolymer is considered as the third generation cement. The term 'geopolymer' is generically used to describe the amorphous to crystalline reaction products synthesised by aluminosilicates reacted with alkali solution. Different terms such as "Inorganic polymers", "Alkali-activated cements", "Geocements" etc., describe materials synthesized utilizing the same chemistry [4].

A variety of aluminosilicate materials such as kaolinite, industrial by-products such as fly ash and slag have been used as solid raw materials in the alkali activated systems. The reactivity of these aluminosilicate sources depends on their chemical make-up and composition. The alkaline activators such as sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) and potassium silicate ( $\text{K}_2\text{SiO}_3$ ) are used to activate these aluminosilicate materials. Under highly alkaline conditions, reactive aluminosilicates are rapidly dissolved and free  $[\text{SiO}_4]^-$  and  $[\text{AlO}_4]^-$  tetrahedral units are released in the solution. The tetrahedral units are alternatively linked to polymeric precursor by sharing oxygen atom, forming polymeric Si–O–Al–O bonds.

### 2.1 Alkali activated reaction mechanism

There are two models of alkali activation:

- Activation by low to mild alkali of a material like slag containing primarily silicate and calcium. The product will be (C-S-H) gel similar to that is being formed in OPC but with lower Ca/Si ratio.
- The second mechanism involves the activation of a material containing primarily silicates and aluminates like fly ash using a highly alkaline solution. This reaction will form an inorganic binder through polymerization process, and the term geopolymer is used to characterize this type of reaction.

The geopolymer reaction differentiates geopolymers from other types of alkali activated materials (such as alkali activated slag) since the product is geopolymer rather than C-S-H gel. It is reported that the hydration products of metakaolin or fly ash (FA) activation are zeolite type which is sodium aluminosilicate hydrate gels with different Si/Al ratio whereas the major phase produced in slag activation is calcium silicate hydrate with a low Ca/Si ratio. Then many physical properties of geopolymers prepared from various aluminosilicate sources may appear to be similar while their microstructures and chemical properties vary to a large extent.

## 3 FACTORS AFFECTING FRESH AND HARDENED PROPERTIES OF ALKALI ACTIVATED SYSTEMS

Many researches were conducted to gain more fundamental understanding about factors affecting alkali activated systems performance. The following section discuss the most significant factors.

### 3.1 Type of alkali activator

Different types of alkaline activators were used in alkali activated systems such as sodium hydroxide, potassium hydroxide, sodium silicate, sodium carbonates, and etc. [5-7]. The most commonly used activator is sodium hydroxide or a mixture of sodium silicate and sodium hydroxide. The selection of the alkaline activator properties is dominated by the activated material characteristics. Hydration products of alkali activated systems are mostly dependent on activator type and pH value which is the negative log of the hydrogen ion concentration. In case of fly ash, the activation reaction of internal Si and Al components are initiated by the breakage of the glassy chain of fly ash, which is itself provoked by the high alkalinity of the solution. On the other hand, in case of slag activated by sodium hydroxide alone, the product is a semi-crystalline long linear chains of calcium silicate hydrate (C-S-H) with C/S ratio of (0.8 – 1.0). However, slag

activated by water glass, the silicon ions from the alkaline solution initially reacts with the calcium ( $\text{Ca}^{2+}$ ) from the slag forming calcium silicate hydrates with highly condensed anions and low C/S ratio of (0.6 – 0.8). During the alkali activation reaction, the silicate ions which are both dissolved from slag and supplied by the activator provide the system with the necessary species to promote reactions with  $\text{Ca}^{2+}$  ions released from the slag. As the reaction progresses further, the silicate ions supplied by the activator become depleted but slag dissolution continues. Condensation and cross-linking of these species leads to gelation forming C-S-H with a low to moderate Ca/Si ratio [8-10].

### **3.2 Dosage of alkali activator**

Dosage of activator is the amount of sodium oxide  $\text{Na}_2\text{O}$  as a ratio of the binder weight. Generally, the higher the dosage, the better the strength. In geopolymerization, the surface concentration of hydroxide ions directly affect the dissolution rate, which is a function of the bulk concentration of hydroxide ions. Increasing NaOH concentration in the aqueous phase of the geopolymeric system has direct effect on the efficiency of the geopolymerization process. It improves the dissolution rate of Si and Si–Al phases of fly ash, leading to high Si and Al contents in the aqueous phase of geopolymeric systems. This will initiate polycondensation process, which is controlling strength development in geopolymeric materials. While in slag activation, there is a threshold for  $\text{Na}_2\text{O}\%$  dosage depending on slag, activator and curing condition, after which no further significant increase in strength is achieved. Moreover, detrimental properties such as brittleness may increase at higher  $\text{Na}_2\text{O}\%$  dosage as a result of more free alkalis in the product. Trying to increase the strength by increasing the alkali dosage is not recommended from both economic and property points of view [11-13].

### **3.3 Alkali activator modulus**

Activator modulus ( $M_s$ ) is the ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  in the activator. In geopolymers, soluble silicate species are necessary for the initiation of oligomers formation which favor polycondensation of geopolymeric products with good mechanical properties. It enriches the aqueous phase of the geopolymeric system with soluble silicate species, which are necessary for the initiation of polycondensation. The relative concentration of silicate anions is presented as a function of weight ratio of  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  in the aqueous solution. Addition of soluble sodium silicates in the aqueous phase of the geopolymeric system increases  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  ratio. This gradually shifts the chemical system to species with larger rings and complex three dimensional polymeric structures providing good mechanical properties [14]. Although high sodium silicates have positive effect on the mechanical properties of the geopolymeric materials, viscosity of the geopolymeric pastes should be taken in consideration. Viscosity of the aqueous phase was found to increase substantially at high  $\text{SiO}_2$  to  $\text{Na}_2\text{O}$  ratios. This would result in a low workability affecting the hardened mechanical properties [15]. While in slag activation, as the formation of silica gel makes a significant contribution to strength, there is an obvious interaction between activator modulus ( $\text{SiO}_2/\text{Na}_2\text{O}$ ) and  $\text{Na}_2\text{O}$  content. If the  $\text{Na}_2\text{O}$  content is kept constant, the alkaline activation effect can be considered the same for activators with different modulus, the higher the modulus the more the contribution from silica gel and the higher the strength within a certain range of silica content. However, if the waterglass solid content is kept constant, the higher the modulus the lower the  $\text{Na}_2\text{O}$  content and the smaller the alkaline activation effect but the greater is the amount of silica gel. These competing effects result in a variable optimum modulus, depending on the slag fineness and curing condition.

### 3.4 Water content

As alkali activator might be used in solid form, it is more reasonable to consider liquid/solid ratio (l/s). Similar to OPC, increasing w/b ratio to insure the fluidity required for shaping results in a strength reduction. Increasing the l/s ratio results in an increase of alkaline activation due to the introduction of more alkaline component and a simultaneous increase of pore volume in hardened concrete due to introducing more water. Therefore, the effects of l/s ratio on strength are positive at lower l/s ratio where alkaline activation is a dominant factor.

## 4 DURABILITY OF ALKALI ACTIVATED MATERIALS

One of the major problems associated with OPC concrete is its long term performance against aggressive environments. The deterioration of concrete is usually assessed for sulphate attack, chloride induced corrosion, atmospheric carbonation, alkali-silica reaction. A lot of studies had been carried out to understand the behaviour of alkali activated materials exposed to these conditions.

### 4.1 Acid attack

During acid attack to concrete, the extent of degradation depends on the concentration of acid solution and length of exposure period [16]. The resistance is measured in terms of weight loss, reduction in compressive strength and changes of the microstructure (depolymerisation of the aluminosilicate network). Bekharev et al. [17] reported 33% reduction in strength of slag based concrete compared to 47% in OPC concrete when exposed in acetic acid solution of (pH =4) for 12 months. The slag particles and low calcium C-S-H with average Ca/Si ratio of 1 were more stable in the acid solution than of the OPC pastes. During immersion in 2% sulfuric acid ( $H_2SO_4$ ) solution, for 40 MPA slag based concrete, the strength loss was 11% compared to 36.2% for OPC concrete. For metakaolin based geopolymer, tested pastes by Davidovits et al. [18] exhibited only 7% mass loss when immersed in 5%  $H_2SO_4$  for 30 days. It was also reported that fly ash-based geopolymer pastes retained a dense microstructure after 3 months exposure in nitric acid ( $HNO_3$ ).

### 4.2 Sulfate attack

The mechanism of sulfate attack on OPC concrete usually involves tricalcium aluminate ( $C_3A$ ) and portlandite in the cement matrix and sulfate ions [19]. Sulfate ions reacts with portlandite to form gypsum, which then react with the hydration products of  $C_3A$  to form ettringite. This final product was reported to cause expansion, leading to concrete failure [20-22].

In alkali activated materials, sulfate attack is mainly destroying the aluminosilicate skeleton. Several attempts [6, 23-25] have been made to study sulfate resistance of alkali activated materials. The deterioration in concrete was evaluated in terms of visual appearance, weight loss and loss of compressive strength. Generally, alkali activated materials using NaOH had shown the best performance than those made with sodium silicate and (NaOH/KOH). This might be attributed to the more stable cross-linked aluminosilicate structure when using NaOH [16].

Hardjito et al. [6] reported that there was no significant loss in compressive strength or weight of fly ash based concrete submerged in 5%  $Na_2SO_4$  for three months. Thokchom et al. [25] tested geopolymer mortar specimens manufactured by activating low calcium fly ash with a mixture of sodium hydroxide and sodium silicate solution. He reported that specimens surfaces received white deposits (flaky and elongated white deposits) throughout the duration of exposure. This deposits were more observed as the  $Na_2O$  content increased. He also reported a variation of pH value of the sulfate solution. The increase in pH may be attributed to migration of alkalis from specimen into the solution as reported by Bakharev [23]. The residual compressive strength after 24 weeks of exposure to 10% magnesium sulfate solution was varying with the  $Na_2O$  content. The more the  $Na_2O$  content, the less the compressive strength loss. Scanning electron microscopy (SEM) and EDX tests showed that according to traces of constituent elements at some spots,

formation of gypsum and ettringite was possible. Localized cracks were noticed which should be attributed to formation of ettringite.

#### **4.3 Alkali silica reaction**

Severe deterioration of hardened Portland cement concrete is gradually caused by Alkali-silica reaction in terms of strength loss, cracking and volume expansion. It takes place through reaction between the hydroxyl ions in the pore solution within the concrete matrix and reactive silica of the aggregate. This reaction is generally occurs in stages. In the first stage, the hydrolysis of reactive silica react with hydroxyl ions to form alkali-silica gel, then absorption of water by the gel will result in a volume increase [26]. In geopolymer concrete, the unutilized alkali after geopolymerization of aluminosilicates is expected to react with the silica of the aggregates causing disruption to bridging process. Geopolymers with aggregates of different reactivity were reported to achieve less expansion relative to Portland cement mortars [27]. Fly ash based geopolymers generally exhibit no significant expansion. This is attributed to the formation of crystalline zeolites which is very slow and minerals are usually found in the gaps of the matrix, then stress that might generate cracking is unlikely [28]. For slag based mortars, in comparison to OPC, AAS shows expansion less than 0.05 % which is lower than OPC. This might be attributed to the presence of portlandite in OPC which favors ASR because it provides  $\text{Ca}^{2+}$  ions in solution. Conversely, in AAS, alkalis are parts in different reaction products as CSH formed with low Na and Al content. Therefore, a competition between the slag and ASR is established. This factor, together with the absence of free  $\text{Ca}^{2+}$  ions, justifies the low expansion of the AAS mortars stored in water compared to OPC mortars. The same initial reactions take place when test is accelerated through storing mortars in NaOH solution. However, the reaction takes longer time (more than 16 days). At high alkali content, a second reaction products (sodium and calcium silicate hydrate gel) is formed inducing expansion, which explain why accelerated test is not suitable for AAS [29].

#### **4.4 Carbonation and permeability**

Carbon dioxide is always around and capable to penetrate to concrete and dissolve in pore water forming carbonic acid. The carbonic acid that forms in the concrete's pores reacts with portlandite (CH) and produces calcium carbonate.

This process basically replaces the relatively large CH molecules with relatively small calcium carbonate molecules. This replacement increases concrete's porosity and decreases its pH. Although concrete absolute volume may remain the same, the increase in porosity reduces this desirable product's relative volume and decreases its strength.

The most significant effect of carbonation on concrete is reducing its durability through reducing its pH. The highly alkaline environment of concrete, which usually has a pH in excess of 12, creates a protective, passivating oxide layer around steel, protecting the reinforcement from corrosion. Carbonation is capable of reducing a concrete pH to a value less than 9, which significantly weakens, or even eliminate, the steel's protective layer [30]. This reduction in pH can be simply explained as follow: Calcium hydroxide contains two hydrogen ions while calcium carbonate contains zero hydrogen ions. After some of the calcium hydroxide is consumed during the carbonation process and partially replaced by calcium carbonate, hydrogen ions still exist in the matrix but at a lower concentration. The weaker hydrogen ion concentration reduces concrete pH leading to steel corrosion. Highly permeable concrete, as a result of cracks or excessive porosity, has an increased likelihood for carbonation.

Olivia et al. [31] reported low water permeability of fly ash based geopolymer concrete cured at 60 °C for 24 h compared to that of the OPC concrete due to its denser paste and smaller pore inter-connectivity. Bernal et al. [32] studied slag/metakaolin-based concretes (water to binder ratio (w/b)= 0.47) under an accelerated carbonation test. They reported that the compressive strength decreased as the carbonation proceeds. It is important to notice that the relationship between the pore volume and extent of carbonation was much more similar with samples with different percentages of metakaolin contrary to the slag-based samples. This can be attributed to calcium carbonate formation in both types of concrete proving that porosity is not the only factor causing strength loss.

## 5 FIRE BEHAVIOR OF ALKALI ACTIVATED MATERIALS

Ordinary Portland cement concrete has adequate fire resistance. However, it loses almost 70 % of its original strength when exposed to 1000 °C. This loss of strength might be attributed to dehydration and destruction of C-S-H and other crystalline hydrates. As a result of high temperature gradient, hotter external exposed layers are tending to separate and spall from the cooler interior [33]. In geopolymers, good fire resistance at elevated temperature is logic since the highly distributed nano pores allowing physically and chemically bonded water to evaporate without damaging the aluminosilicate network [4]. Residual strength of geopolymers was reported to increase by 6% that the original strength [34]. This increase might be attributed to the sintering reaction of unreacted fly ash particles possessing higher spalling resistance under fire than the OPC concrete.

## 6 CONCLUSION

Waste materials which are rich with aluminosilicates attracted the researchers attention to make a benefit of its recycling to produce the third generation of binders. Besides that, they achieved the concept of green concrete through lowering the CO<sub>2</sub> emission, the industrial energy consumed by OPC production processes and raw material resources attrition as well. Alkali activated materials are generally produced by activation of aluminosilicates sources using alkali solutions (activator). Among many types of activators, sodium hydroxide and sodium silicates were found to be the best activators that gives the best properties of alkali activated systems. Two mechanisms of reaction for alkali activated systems were identified, the first is Activation of material containing primarily silicate and calcium and the product is (C-S-H) gel similar to that is being formed in OPC but with lower Ca/Si ratio. The second to activate a material containing primarily silicates and aluminates, reaction will form an inorganic binder through polymerization process, and the term geopolymer is used to characterize this type of reaction. Slag and fly ash were found to be the most suitable raw materials for alkali activated systems, taking in consideration the different reaction mechanism and the different product nature as well.

There are a lot of factors that affect the properties of alkali activated systems such as type of activator, dosage of alkali activator, activator modulus and water content or liquid to solid ratio. Deterioration of concrete is usually related to the exposure to aggressive environments, alkali activated systems were tested with the exposure to simulated aggressive environments to state its convenience for implementation in construction industry. In addition, alkali activated systems had proved good fire resistance comparing to OPC which already has adequate resistance to fire.

## 7 REFERENCES

1. Mehta, P.K. and S.C.M.f.S. Development, High-performance, high-volume fly ash concrete: materials, mixture proportioning, properties, construction practice, and case histories. 2002: Supplementary Cementing Materials for Sustainable Development.
2. Costello, A., et al., Managing the health effects of climate change: lancet and University College London Institute for Global Health Commission. The Lancet, 2009. 373(9676): p. 1693-1733.
3. Hendriks, C.A., et al. Emission reduction of greenhouse gases from the cement industry. in Proceedings of the fourth international conference on greenhouse gas control technologies. 1998. Interlaken, Austria, IEA GHG R&D Programme.
4. Duxson, P., et al., Geopolymer technology: the current state of the art. Journal of materials science, 2007. 42(9): p. 2917-2933.
5. Fernández-Jiménez, A. and A. Palomo, Composition and microstructure of alkali activated fly ash binder: Effect of the activator. Cement and concrete research, 2005. 35(10): p. 1984-1992.

6. Hardjito, D., et al., On the development of fly ash-based geopolymer concrete. *Materials Journal*, 2004. 101(6): p. 467-472.
7. Palomo, A., M. Grutzeck, and M. Blanco, Alkali-activated fly ashes: a cement for the future. *Cement and concrete research*, 1999. 29(8): p. 1323-1329.
8. Fernández-Jiménez, A., et al., Structure of calcium silicate hydrates formed in alkaline-activated slag: influence of the type of alkaline activator. *Journal of the American Ceramic Society*, 2003. 86(8): p. 1389-1394.
9. Wang, S.-D. and K.L. Scrivener, Hydration products of alkali activated slag cement. *Cement and Concrete Research*, 1995. 25(3): p. 561-571.
10. Wang, S.-D. and K.L. Scrivener, <sup>29</sup>Si and <sup>27</sup>Al NMR study of alkali-activated slag. *Cement and Concrete Research*, 2003. 33(5): p. 769-774.
11. Metso, J. and E. Kajaus, Activation of blast furnace slag by some inorganic materials. *Special Publication*, 1983. 79: p. 1059-1074.
12. Parameswaran, P. Alkali Activation of India Blast Furnace Slag. in *Proceedings, 8th International Congress on Chemistry of Cement*, Rio de Janeiro. 1986.
13. Wang, S.-D., K.L. Scrivener, and P. Pratt, Factors affecting the strength of alkali-activated slag. *Cement and concrete research*, 1994. 24(6): p. 1033-1043.
14. Falcone, J.S., *Soluble silicates*. Vol. 194. 1982: American Chemical Society.
15. Papias, D., I.P. Giannopoulou, and T. Perraki, Effect of synthesis parameters on the mechanical properties of fly ash-based geopolymers. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2007. 301(1-3): p. 246-254.
16. Singh, B., et al., Geopolymer concrete: A review of some recent developments. *Construction and building materials*, 2015. 85: p. 78-90.
17. Bakharev, T., J. Sanjayan, and Y.-B. Cheng, Resistance of alkali-activated slag concrete to acid attack. *Cement and Concrete Research*, 2003. 33(10): p. 1607-1611.
18. Davidovits, J., *Geopolymers: inorganic polymeric new materials*. *Journal of Thermal Analysis and calorimetry*, 1991. 37(8): p. 1633-1656.
19. Rozière, E., et al., Durability of concrete exposed to leaching and external sulphate attacks. *Cement and Concrete Research*, 2009. 39(12): p. 1188-1198.
20. Cohen, M., Theories of expansion in sulfoaluminate-type expansive cements: schools of thought. *Cement and Concrete Research*, 1983. 13(6): p. 809-818.
21. Mehta, P.K., Mechanism of sulfate attack on portland cement concrete—Another look. *Cement and Concrete Research*, 1983. 13(3): p. 401-406.
22. Odler, I. and M. Gasser, Mechanism of sulfate expansion in hydrated Portland cement. *Journal of the American Ceramic Society*, 1988. 71(11): p. 1015-1020.
23. Bakharev, T., Durability of geopolymer materials in sodium and magnesium sulfate solutions. *Cement and Concrete Research*, 2005. 35(6): p. 1233-1246.
24. Rajamane, N., et al., Sulphate resistance and eco-friendliness of geopolymer concretes. *Indian Concrete Journal*, 2012. 86(1): p. 13.
25. Thokchom, S., P. Ghosh, and S. Ghosh, Performance of fly ash based geopolymer mortars in sulphate solution. *Journal of engineering science and technology review*, 2010. 3(1): p. 36-40.
26. Hester, D., C. McNally, and M. Richardson, A study of the influence of slag alkali level on the alkali-silica reactivity of slag concrete. *Construction and Building Materials*, 2005. 19(9): p. 661-665.
27. Kupwade-Patil, K. and E.N. Allouche, Impact of alkali silica reaction on fly ash-based geopolymer concrete. *Journal of materials in Civil Engineering*, 2012. 25(1): p. 131-139.

28. García-Lodeiro, I., A. Palomo, and A. Fernández-Jiménez, Alkali–aggregate reaction in activated fly ash systems. *Cement and Concrete Research*, 2007. 37(2): p. 175-183.
29. Fernández-Jiménez, A. and F. Puertas, The alkali–silica reaction in alkali-activated granulated slag mortars with reactive aggregate. *Cement and concrete research*, 2002. 32(7): p. 1019-1024.
30. Leelalerkiet, V., et al., Analysis of half-cell potential measurement for corrosion of reinforced concrete. *Construction and Building Materials*, 2004. 18(3): p. 155-162.
31. Olivia, M. and H. Nikraz, Properties of fly ash geopolymer concrete designed by Taguchi method. *Materials & Design (1980-2015)*, 2012. 36: p. 191-198.
32. Bernal, S.A., R.M. de Gutiérrez, and J.L. Provis, Engineering and durability properties of concretes based on alkali-activated granulated blast furnace slag/metakaolin blends. *Construction and Building Materials*, 2012. 33: p. 99-108.
33. Neville, A.M., *Properties of concrete*. Vol. 4. 1995: Longman London.
34. Dattatreya, J., et al., Flexural behaviour of reinforced Geopolymer concrete beams. *International Journal of civil and structural engineering*, 2011. 2(1): p. 138.