

Some Progresses in the Challenges for Geopolymer

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Abstract. Geopolymer is manufactured by chemical activation of industrial by-products, which include blast furnace slag, fly ash, steel slag, phosphorus slag etc, with alkali activators, such as the sodium silicate, sodium carbonate and sodium hydroxide and their mixtures. It has attracted worldwide attention due to its advantages of simple production process, low energy consumption, effective utilisation of industrial by-products and reduction of greenhouse gas emissions. However, as materials vary substantially in physicochemistry properties, hardening, workability and durability of deriving geopolymer products vary accordingly. Slag-based geopolymer usually set within a very short period of time (less than 30 min), while low calcium fly ash-based geopolymer takes long time (a couple of days) to set. Geopolymer binders cured at room temperature exhibited significantly higher shrinkage than Portland cement does, while thermal cured products are very volumetrically stable. Moreover, alkali-aggregate reaction can happen when alkali-reactive aggregates are used with geopolymer binders. These issues need to be considered in large scale applications. This paper reviews the current advance in the research of geopolymer.

1. Introduction

With demand driven by environmental protection and waste utilisation, geopolymers have been developed rapidly in past decades for the potential as alternatives to Portland cement (PC) [1]. These materials can be manufactured through the reaction of an aluminosilicate-normally in powder form of industrial by-products such as blast furnace slags, fly ash or heated clay, with an alkaline activator, which is usually a concentrated aqueous solution of sodium hydroxide, silicate, carbonate or sulfate [2]. Properly designed geopolymers behave much better than PC in many durability aspects, such as chemical attack, thermal stability and fire resistance [3-5].

Plenty of studies were concentrated on the nature, performance and application of geopolymers. Shi et al. [2] summarised the research achievements of geopolymeric cements and concretes before the year of 2005. Shi and Polamo et al. [1] discussed the chemistry of alkali-activated binder systems, and firstly classified geopolymers into five categories: 1) alkali-activated slag-based cements; 2) alkali-activated pozzolan cements; 3) alkali-activated lime-pozzolan/slag cements; 4) alkali-activated calcium aluminate blended cements; and 5) alkali-activated Portland blended cements. Provis and Shi et al. [4] reviewed and highlighted the recent key scientific developments in the development, characterization, durability, processing and environmental assessment of geopolymers. All the works identified the importance for future research and development to support the optimal and appropriate utilisation of geopolymer as a component of a sustainable future construction materials industry.



Nevertheless, hydration or reaction mechanisms of geopolymer are much more complicated when compared to that of PC. The type of raw material, dosage of activator and curing conditions all have significant impact on the reaction process and microstructure characteristics of hardened products, making geopolymers more complicated to understand satisfyingly. There is no universal strength evaluation or design criteria developed yet [6]. Because of the variation of raw materials, geopolymer prepared by different researchers showed large differences in performance. For example, the setting time of geopolymer is one of the important factors affecting its practical application. It determines the time window for mixing, transportation and casting of concrete. However, setting time of slag-based geopolymer is usually much shorter than traditional PC cement [6].

Also, the drying shrinkage of slag-based geopolymer is larger due to the characteristics of hydration products C-S-H gels and the finer pore structure [2]. In terms of alkali-aggregate reaction (AAR) of geopolymer, some researchers believed that AAR will not occur or less likely in geopolymeric binders compared to PC [7]; on the other hand, thought that the possibility of AAR occurring in slag-based geopolymer was higher [8]. At present, there is no consistent conclusion in these aspects. In this paper, advances in research of reactivity index of precursors, setting time, shrinkage and alkali-aggregate reaction of geopolymers are presented.

2. Reactivity index of precursors

Some demonstration projects have been constructed using geopolymer concretes made from alkali activated fly ash blended with certain proportions of slag [9]. However, large-scale manufacture of geopolymer still progresses slowly and faces some technical and regulatory obstacles [10]. Among these, the inconsistent properties of slag and fly ash (between sources, and from time to time from a single source) may be the most critical issue hindering large-scale deployment. To solve this problem, it is necessary to construct effective assessment methods to determine the performance of slags and fly ashes in geopolymer mixes and predict their likely strength development based on readily-assessed material parameters.

Slag is relative consistent in composition, and extensive studies have been conducted on slag-based geopolymer. Shi et al. [2] summarized the hydraulic reactivity index of slag used in PC-based cement (Table 1). These formulas are divided into three types: Type I considers the amount of SiO₂ (a main component in slag). K3 generally is used as an index approach to evaluate the reactivity of slag in many countries, and that generally need to >1.0 according to European and Canadian standards, whereas, >1.4 according to Japanese standards. K7 is applied to the certain type of slag with high MgO content; Type II considers the influence of some secondary components, such as TiO₂ and MnO. K11 is usually >1.2 according to Chinese standard; Type III indicates that Al₂O₃ has a negative impact on the hydraulic reactivity of slag. K12 is proposed according to the 28 d strength, while K13 is proposed according to the strength after 28 d.

In addition, Duxson and Provis [11] found that the reactivity of slag particles is largely controlled by the degree of depolymerization (DP) which is calculated from free Si/free Ca, assuming that all the Mg present is in akermanite (2CaO·MgO·2SiO₂) and all the Al in gehlenite (2CaO·Al₂O₃·SiO₂). Materials with a DP of about 1.3-1.5 are generally considered to have high extent of depolymerisation.

$$DP = \frac{\text{Free Ca}}{\text{Free Si}} = \frac{\text{Total Ca} - \text{Ca in gehlenite} - \text{Ca in akermanite} - \text{Ca associated with S}}{\text{Total Si} - \text{Si in gehlenite} - \text{Si in akermanite}} \quad (1)$$

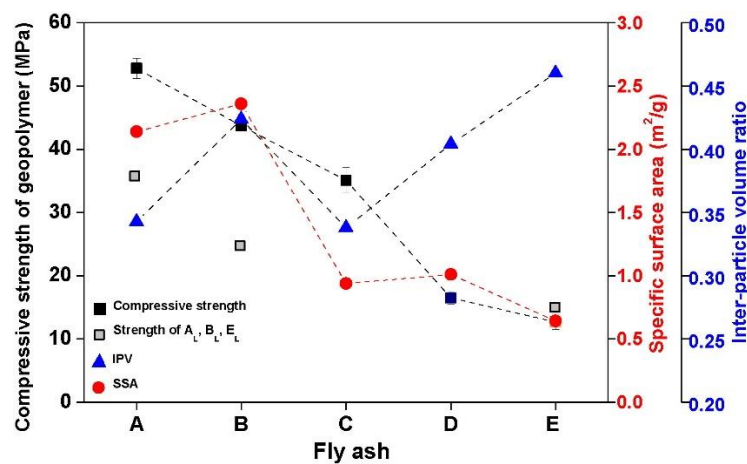
However, fly ashes behave significantly different in terms of the chemical and physical characteristics due to variations in the features of coal sources, and the combustion processes applied in different facilities worldwide. Recently, Zhang et al. [12] proposed an equation to simply link all of the factors such as particle size, specific surface area, initial packing density and chemical compositions. Applying the developed reactivity index to evaluate the fly ashes in selected literature studies of geopolymer manufacture can show the powerful capability of this approach.

Table 1. A summaries of hydraulic reactivity index of slag used in PC cement.

Type	Hydraulic reactivity index	
I	$K1 = 100 - SiO_2$	$K2 = \frac{100 - SiO_2}{SiO_2}$
	$K3 = \frac{CaO + MgO + Al_2O_3}{SiO_2}$	$K4 = \frac{CaO + MgO + Al_2O_3 - 10}{SiO_2}$
	$K5 = \frac{CaO + 1.4MgO + 0.6Al_2O_3}{SiO_2}$	$K6 = CaO + 0.5MgO + Al_2O_3 - 2.0SiO_2$
	$K7 = \frac{6CaO + 3Al_2O_3}{4MgO + 7SiO_2}$	
	$K8 = \frac{CaO + 0.5MgO + CaS}{SiO_2 + MnO}$	$K9 = \frac{CaO + 0.5MgO + Al_2O_3}{SiO_2 + FeO + (MnO)_2}$
II	$K10 = \frac{CaO + MgO + Al_2O_3 + BaO}{SiO_2 + MnO}$	$K11 = \frac{CaO + MgO + Al_2O_3}{SiO_2 + MgO + TiO_2}$
III	$K12 = \frac{CaO + MgO + 0.3Al_2O_3}{SiO_2 + 0.7Al_2O_3}$	$K13 = \frac{CaO + MgO}{SiO_2 + 0.5Al_2O_3}$

$$I = \frac{SSV}{IPV} \times \frac{\text{total charge of network modifiers } (C_{NM})}{\text{molar number of network formers } (n_{NF})} \quad (2)$$

Where, SSA is specific surface area, IPV is inter particle volume. It is reasonable to believe that such a comprehensive index can prove to be a powerful tool in evaluating and grading the suitability of fly ashes for geopolymer formulation. However, more efforts are necessary to specify the relative contribution of each parameter to further refine the index equation.

**Figure 1.** The relationship between fly ash specific surface area (SSA), interparticle volume ratio (IPV) and compressive strengths of the geopolymers obtained from five different ashes [12].

3. Setting

The setting time of geopolymer is one of the important performances that affects practical application. It determines the time window for mixing, transportation and casting of concrete. However, fast-setting is a feature of slag-based geopolymer. The setting time of slag-based geopolymer is generally less than 30 min [6]. The setting behaviour is affected by many factors, such as raw material selection, specimen preparation and process conditions, and other additives. Most chemical retarders for PC are not compatible in geopolymers [13]. Borates and phosphates are considered suitable but may reduce the compressive strength of geopolymer while increase the cost as low dose is not effective.

Li and Shi et al. [14] found that the setting time of slag-based geopolymer is prolonged with increased fly ash or metakaolin as show in Figure 2. There was a similar tendency in setting time for alkali-activated slag-fly ash and alkali-activated slag-metakaolin. Structurally slag was aluminosilicate glass with covalent bonds of Si-O, Al-O and Ca-O. The bond energy of Si-O, Al-O and Ca-O are 444, 221-280 and 134 kJ/mol, respectively [15]. Thermodynamically, the first step under the alkaline activation conditions was the breaking of Ca-O bonds, releasing Ca^{2+} , followed by gradual breaking of Al-O and then Si-O bonds. With the rapid release and accumulation of Ca^{2+} , calcium rich aluminosilicate gels formed and precipitated, leading to the initial setting. Therefore, the high concentration of CaO in slag was the main reason for shortening the setting time. In comparison, metakaolin and Class F fly ash contained Si-O and Al-O bonds in majority. The dissolution of the bulk metakaolin particle is slower than slag because of the lack of active 'Ca-O bonds'. The alkali-activated metakaolin, spatially fly ash, usually requires high concentration of alkaline solution and high temperature curing to break down the Si-O and Al-O bonds, which further polymerized into gels or semi to full-crystallized products [15, 16]. Li and Shi et al. [6] further summarized the setting times of slag-based geopolymer formed by activation of precursor in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ systems with the same activator (modulus = 1.4) in Figure 3. A general trend can be observed that the setting time decreased with the increase of CaO content in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ systems.

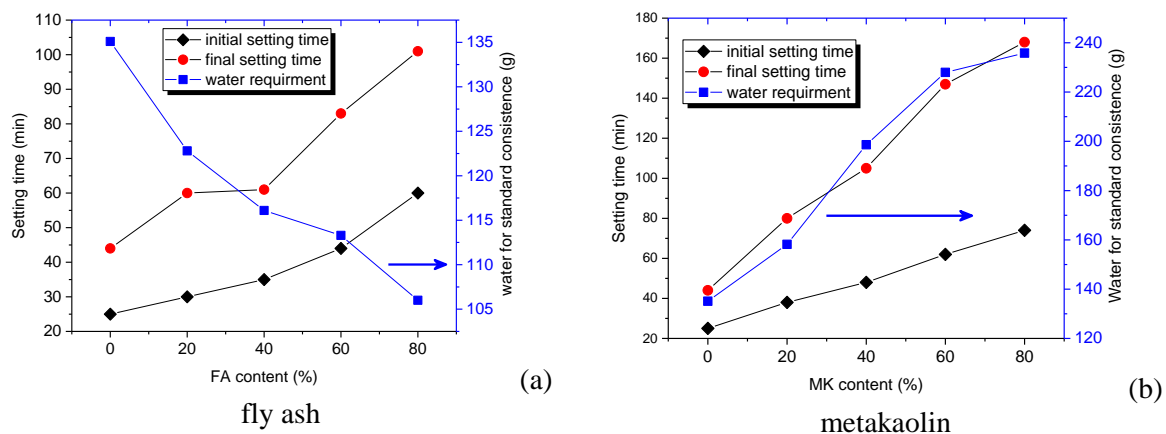


Figure 2. Effect of fly ash and metakaolin contents on initial and final setting time of slag-based geopolymer [14].

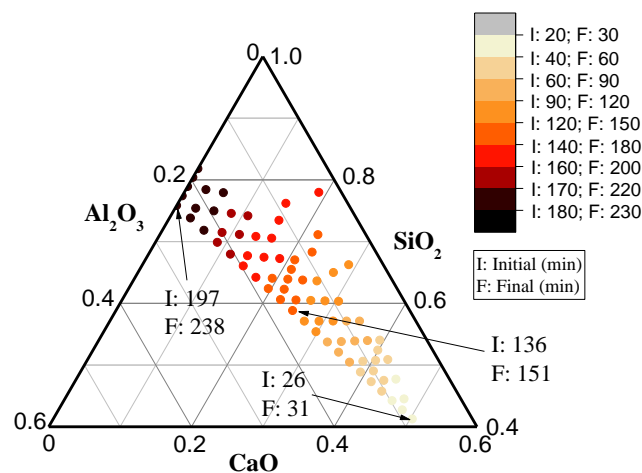


Figure 3. Setting times of geopolymer in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ solid precursor system [6].

Control of activator is another option to adjust setting time of geopolymer in addition to adding mineral admixtures. Shi et al. [17] and Bernal et al. [18, 19] illustrated that a prolonged induction period, which can take up to 3-5 days in some slag-based geopolymer systems, can be obtained when carbonate is used as activator. They showed that the Na_2CO_3 promotes formation of calcite and mixed sodium-calcium carbonates prior to C-(A)-S-H; and also the reduced pH when using this activator slows down the initial dissolution of the slag [17]. Li et al. [14] further investigated that the setting time of alkali-activated slag with Na_2CO_3 - NaOH - Na_2SiO_3 ternary activators (Figure 4). The setting time is prolonged with the increase of Na_2CO_3 content, especially on final setting time. The initial setting time of Na_2CO_3 -slag is more than 300 min while the final setting time is about 6 days. The similar results also were showed in the works by Jimenez et al. [20] (mortar setting time above 3d), Kovtun et al. [21] (concrete setting time about 8h) and Atis et al. [22] (paste setting time about 3h). Proper mix of Na_2CO_3 , $\text{Na}_2\text{O}\cdot\text{rSiO}_2\cdot\text{nH}_2\text{O}$, and NaOH can take advantage of respective anion groups, leading to a reasonable setting time, workability and compressive strength as well [23].

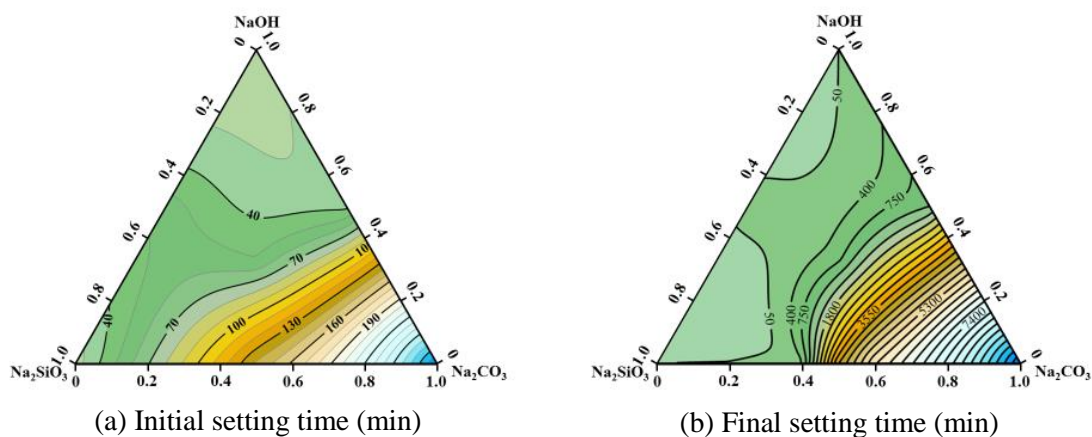


Fig. 4. Setting time contours of slag-activated with Na_2CO_3 - NaOH - Na_2SiO_3 [14].

4. Shrinkage

Shrinkage of geopolymer is a critical issue for its industrial application. Many studies [2, 24, 25] have shown that slag-based geopolymer exhibited much higher shrinkage than PC at early age. The shrinkage of geopolymer was found to be closely related to the nature and microstructural characteristic of the activation products of geopolymer [26]. Thomas et al. [27] found that slag-based geopolymer was likely to undergo twice as much chemical shrinkage and larger autogenous shrinkage as compared to PC-based system. It has been reported that higher drying shrinkage was observed in geopolymer concrete than PC concrete, even though more moisture was lost during the shrinkage measurement for the latter age.

The addition of fly ash is considered to effectively reduce the dry shrinkage of geopolymer; however, an opposite result was reported by some studies [28]. Hu et al. [29] recommended that the addition of fly ash would reduce the autogenous shrinkage and dry shrinkage of geopolymer due to the combination of activity effect, micro aggregate effect and the morphological effect of fly ashes as shown in Figure 5. With the increases of fly ash content, the shrinkage of geopolymer is decreased, especially on drying shrinkage.

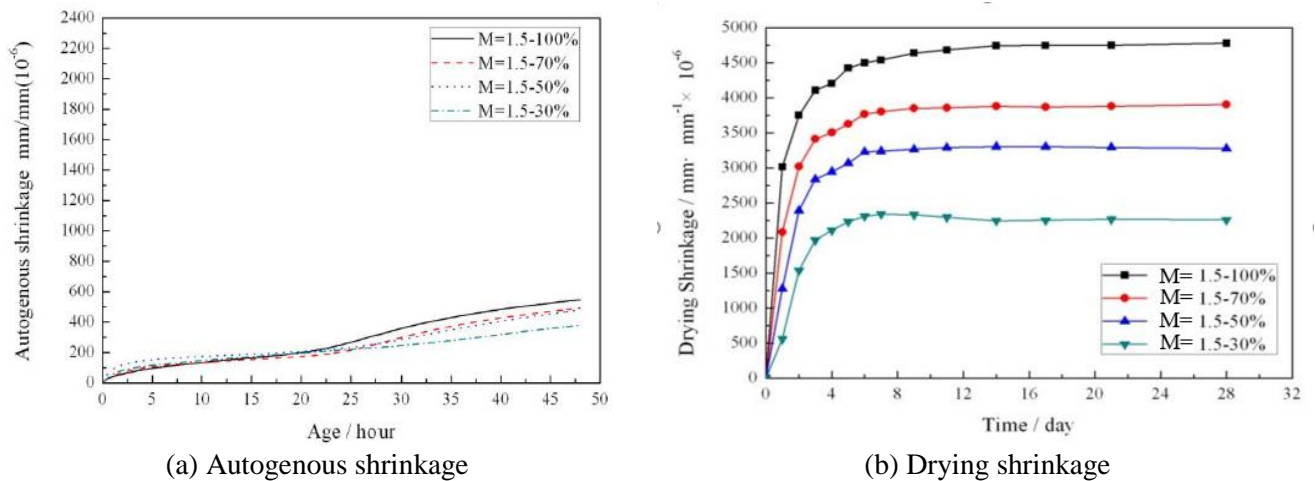


Fig. 5. Autogenous shrinkage and drying shrinkage of alkali-activated slag-fly ash with different slag content [29].

In addition, expansive and shrinkage reducing agents are often used for shrinkage control. However, they may significantly decrease the strength of geopolymer. Hu et al. [30] found that the drying shrinkage of alkali-activated slag mortars showed identical dependence on modulus of sodium silicate, regardless of the chemical admixture addition (Figure 6). For PC concrete, shrinkage reducing agent and MgO are both effective i. Shrinkage reducing agent significantly decreased the drying shrinkage of geopolymer mortars by decreasing the capillary tension within pastes. However, the swelling effect of MgO was limited due to the compact pore structure of geopolymer mortars. The addition of fly ash or shrinkage reducing agent is considered to be effective towards reduction of dry shrinkage of geopolymer products.

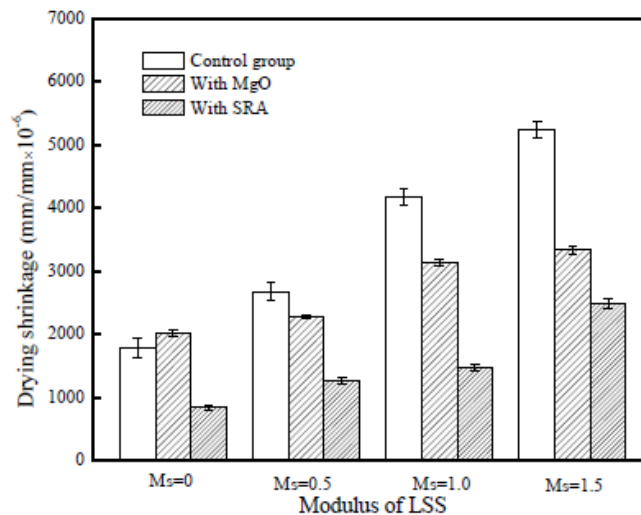


Fig. 6. Influence of chemical admixtures on drying shrinkage of alkali-activated slag mortars [30].

Based on previous work, Hu et al [30] found that the relationships of autogenous and drying shrinkage of alkali-activated slag mortars and exposure ages were well expressed by exponential regression equations, as shown below, showed the higher fitting degree:

$$\varepsilon_s(t) = \varepsilon_{s,\infty}(1 - ae^{bt}) \quad (3)$$

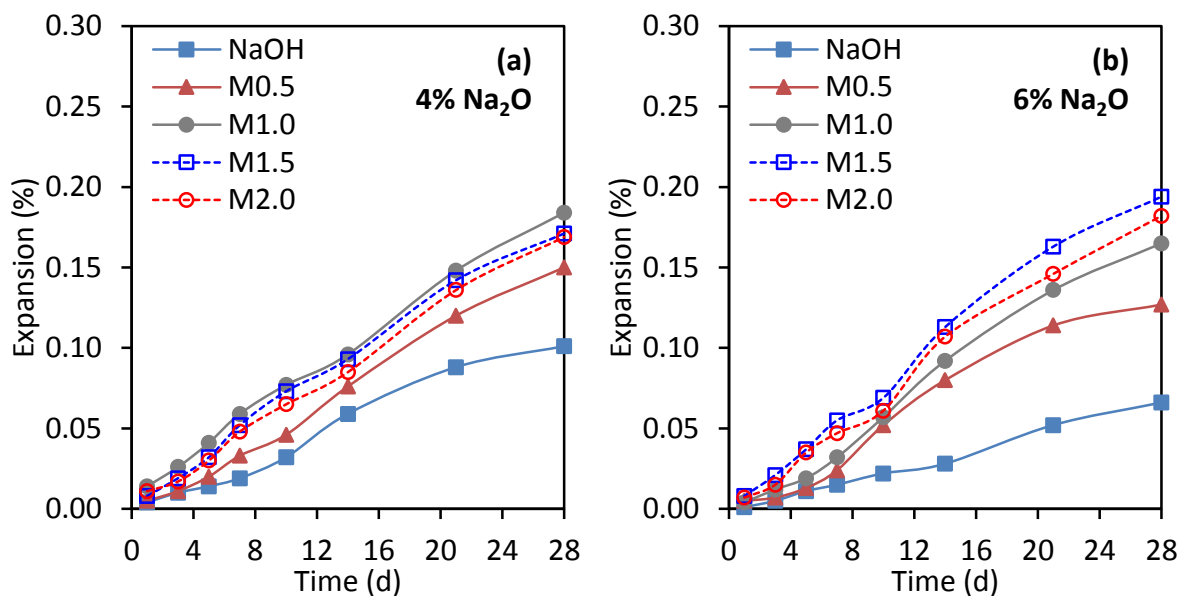
Where $\varepsilon_s(t)$ is the autogenous shrinkage or drying shrinkage strain (microstrain) after age t , $\varepsilon_{s,\infty}$ represents the overall value of autogenous shrinkage or drying shrinkage (microstrain); a and b are constant factors; t is the testing age (hour or day). The exponential Equation 3 can be used to describe the relationships between autogenous shrinkage or drying shrinkage and ages and shrinkage development of alkali-activated slag mortars.

Since high shrinkage has become one of the biggest obstacles for the development and applications of geopolymer, extensive investigations on shrinkage reduction are highly demanded.

5. Alkali-aggregate reaction

Mitigation of alkali-aggregate reaction (AAR) in concrete is essential for durable and sustainable constructions. Geopolymer shows different mechanisms and performance from PC samples in AAR. Alkali content in geopolymeric binders usually exceeds 3%, while it is usually less than 0.5% in PC. In addition, AAR depends much on the actual effective alkali content in cement. The lack of calcium hydroxide decreases the concentration of calcium ion in pore solution of geopolymer [31, 32], and C-S-H with low C/S ratio may “immobilize” more alkali ions than that with high Ca/Si ratio.

Some studies reported that AAR expansion increased with the increase of alkali dosage [33-35], and others reported that AAR expansion decreased with the increase of alkali dosage [36]. Shi et al. [37] showed that NaOH activated slag mortars have lower expansion compared to the AAS mortars activated by waterglass at a given alkali dosage. For all the studied AAS mortars, the expansions are relatively lower compared to those of Portland cement mortars containing the same aggregates under the same exposure conditions [38]. The results suggest a high AAR resistance of the AAS mortars than Portland cement mortars under the accelerated mortar bar testing conditions. However, care should be kept in mind that the risk of AAR may be higher for AAS mortars than Portland cement mortars under natural condition due to the high pore alkalinity of the AAS mortars as discussed in previous study [36].



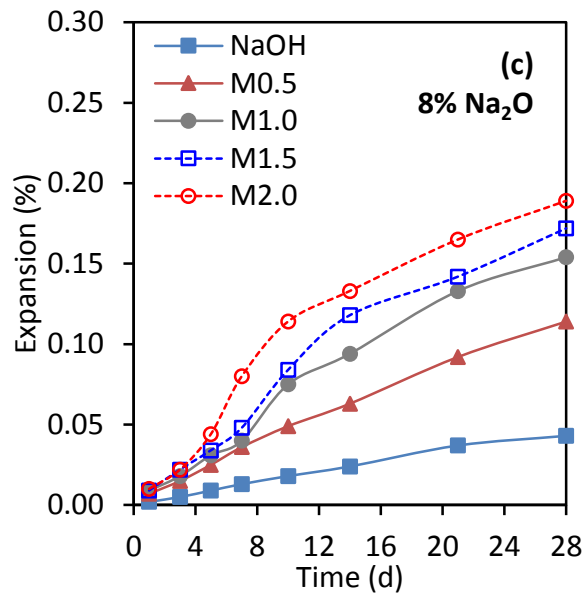


Figure 7. Evolution of AAR expansion of the AAS mortars with different alkali dosages and silicate moduli [37].

Recently Shi et al. [39] also investigated AAR in waterglass-activated slag mortars by incorporating fly ash and metakaolin. Both fly ash and metakaolin can mitigate AAR of the waterglass-activated slag mortars. The optimum dosage of the fly ash for controlling the AAR of the alkali-activated mortars is found to be 30%. The expansion decreases with the increase of the amount of metakaolin. The expansion is completely suppressed when the slag is replaced by 70% metakaolin. It is found that the amount of AAR product formed is minor in the studied mortars with highest expansion [39]. The pore solution alkalinity of the studied mortars is the main factor which controls the AAR in the alkali-activated slag mortars. This indicated that supply of external alkalis is necessary in order to promote the extent of AAR, when accelerated mortar bar testing is employed to study AAR in alkali-activated cement-based materials. This means that the suitability of adopting current AAR testing methods (standards) which are based on PC is questionable. Developing more proper durability and performance evaluation standards and specifications for geopolymer materials are demanded.

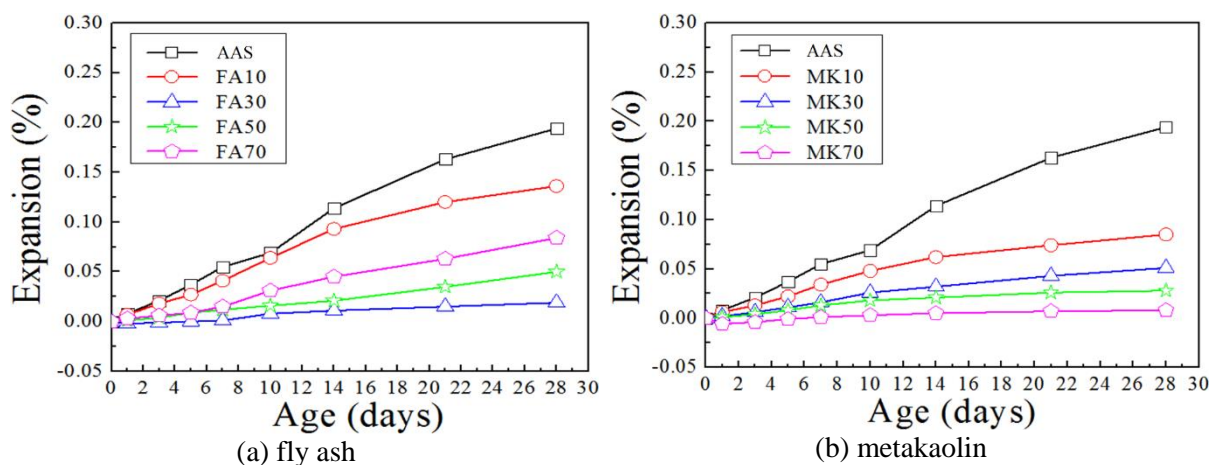


Figure 8. Evolution of AAR expansion of the waterglass-activated slag mortars containing fly ash and metakaolin.

6. Summary

Geopolymers have the charming features of simple production process, low energy consumption, effective utilisation of industrial by-products and reduction of greenhouse gas emission. However, there are many factors influencing the practical performances of geopolymer products. Due to the variation of raw materials, sometimes it is difficult to gain consistent conclusions. Although numerous investigation have already been carried out, issues including reactivity index of precursors, setting time, drying shrinkage and alkali-aggregate reactions need more investigation to facilitate application.

Acknowledgments

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