R. MOHAMED[1,3], R.A. RAZAK[1,2*], M.M. AL BAKRI ABDULLAH[1,3], S.Z. ABD RAHIM[1],
B. KIM[5], T. IMJAI[6], I.H. AZIZ[1], D.L.CH. HAO[1,2]

MONITORING METHODS ON EVOLUTION OF ALKALI ACTIVATION OF ALKALI-ACTIVATED MATERIALS

Alkali activation for producing alkali-activated materials is noted as a complex due to involving several reactions. Due to complexity of the reactions, various techniques have been applied by past researches on monitoring the evolution of alkali-activated materials. The evolution monitored during alkali activation include internal relative humidity, structural evolution, ultrasonic evolution and heat evolution. All of these techniques provide real-time information which is significant for evaluating the reaction process of alkali activation with respected parameters applied thus will be briefly reviewed in this paper. In addition, among those techniques, due to its reliability, heat evolution is one noted as one of the most common techniques applied to elucidate the alkali activation process. Therefore, the potential of heat evolution will also be significantly highlighted in this study.

Keywords: Alkali-activated materials; geopolymer; relative humidity evolution; structural and ultrasonic evolution and heat evolution

1. Introduction

The increment of CO_2 emissions with the increasing demand for OPC production will consequently lead to global warming due to greenhouse gas emissions [1,2]. Alkali-activated materials (AAMs), which include geopolymers, have been offered as alternative binders in the construction field as a result of this concern. AAMs are inorganic polymeric materials composed of silica and alumina (Si and Al) in a three-dimensional network [3,4]. The rich aluminosilicate gel offers advantages in a variety of applications, such as the construction sector, ceramic materials, and even medicine because it serves as a binding material [5,6]. Understanding alkali activation is critical for producing alkali-activated materials with improved properties. This includes optimizing the influencing factors used, such as molarity of sodium hydroxide, alkali activator ratio, and solid-to-liquid ratios [7,8]. As a result, monitoring the evolution of alkali activation is required to see the changes that occur when the influence factors used are varied. Monitoring the evolution can be achieved in a variety of methods, including monitoring the evolution of relative humidity, structural evolution, ultrasonic evolution, and heat evolution. Due to the in-situ approach used to monitor the alkali activation process, each of these technologies provides

real-time information. The evolution of alkali-activated materials is monitored for various duration depending on the method used and the rate of alkali activation. Therefore, this review intends to provide brief information on the evolution methods that have been determined by past researches towards understanding the alkali activation process including geopolymerization.

2. Alkali-activated materials and alkali activation

Alkali activated materials have attracted major research interest worldwide over the past decade towards 'green' materials production. Alkali-activated materials are referred to as an alternative to ordinary Portland cement due to a great potential for lowering carbon dioxide (CO_2) emissions, which are hazardous to the environment and ecology [9,10]. In addition, the easy availability of precursors required in which can be obtained from industrial waste such as steel slag, fly ash and plant-based waste such as rice husk can be denoted as an effort towards minimizing the waste produced by industries [11,12]. Alkali activated materials in which include geopolymers when involving using materials with little or no calcium composition are inorganic polymers typically synthesized via alkali activation (using alkali

[1] UNIVERSITI MALAYSIA PERLIS (UNIMAP), GEOPOLYMER& GREEN TECHNOLOGY, CENTRE OF EXCELLENCE (CEGEOGTECH), PERLIS, MALAYSIA
[2] UNIVERSITI MALAYSIA PERLIS (UNIMAP), FACULTY OF CIVIL ENGINEERING TECHNOLOGY, PERLIS, MALAYSIA
[3] UNIVERSITI MALAYSIA PERLIS (UNIMAP), FACULTY OF CHEMICAL ENGINEERING TECHNOLOGY PERLIS, MALAYSIA
[4] UNIVERSITY OF PLYMOUTH, SCHOOL OF ENGINEERING, COMPUTING AND MATHEMATICS, PLYMOUTH PL4 8AA, UNITED KINGDOM
[5] SCHOOL OF ENGINEERING AND TECHNOLOGY, WALAILAK UNIVERSITY, NAKHORN SI THAMMARAT, 80160, THAILAND

* Corresponding author: rafizarazak@unimap.edu.my

activator) of aluminosilicate precursors (binding materials) thus forming amorphous to semi-crystalline three-dimensional silicon (Si) and aluminum (Al) polymeric networks (-Si-O-Si-, Al-O-Si-) in IV-fold coordination [13-15].

High composition of Al and Si as raw materials for alkali activation are significant since both of these components act as backbone of alkali-activated materials. In addition, the source of raw materials are considered as flexible since any materials with high Si and Al are highly potential to be utilized as raw materials of alkali-activated materials. These materials can be easily obtained from the waste of plants such as fly ash (FA) and ground granulated blast furnace slag (GGBS) and derived from biomass waste such as rice husk ash and palm oil ashes. Meanwhile for liquid precursor, hydroxide solution such as sodium hydroxide (NaOH) is commonly used and usually being combined with silicate solution such as sodium silicate (Na_2SiO_3) for enhancing the reaction process and properties of the alkali-activated materials produced. In order to form alkali-activated materials, there are several chemical reactions occurred during the alkali activation including geopolymerization process. The reactions involved include dissolution of Si and Al species to form monomers, nucleation, gelation and polymerization as well as polycondensation and reorganization process. However, all of these reactions are noted as complex and difficult to observe. Thus, efforts have been made by past researches on monitoring the evolution of early alkali activation (1-3 days) for elucidating the reaction processes occurred in order for better understanding on the properties achieved by alkali-activated materials including strength performance and microstructure properties.

3. Method of monitoring evolution of alkali activation process

Alkali activation process is often referred as complex reaction due to several reaction processes occurred. Therefore, many efforts have been made towards elucidating the significant changes occurred during alkali activation including monitoring the evolution of alkali activation. Some of the monitoring methods are relative humidity evolution [16], structural and phase evolution of metakaolin-based geopolymer [17] and $CaO-FeO_x-SiO_2$ slag [18], ultrasonic evolution of alkali-activated slag [19] and alkali-activated fly ash [19] as well as heat evolution of alkali-activated fly ash [16] and bagasse ash [20]. All of these techniques are capable to be applied for further determination of the reaction kinetics of alkali activation process with the real-time information provided. Some of the past researches focused on monitoring the evolution of alkali activation can be summarized in TABLE 1.

4. Relative humidity evolution

During alkali activation process, during the hardening of alkali-activated materials and geopolymers, internal relative humidity also evolves and commonly related to the shrinkage of the alkali-activated materials produced [21]. The internal relative humidity or simply put as by-products or water content in vapor form due to reactions occurred during the alkali activation process. There is still limited studies available on monitoring the evolution of internal relative humidity during alkali activation and most of the studies commonly focused on the shrinkage effect as being reported by Fang et al. [21] in which aims to provide a better understanding of autogenous shrinkage of alkali-activated fly ash-slag. Ma et al. [22] also reported on monitoring the relative humidity for evaluating the shrinkage of alkali-activated fly ash prepared with different composition of sodium silicate.

A study reported by Hu et al. [16] monitors the evolution of internal relative humidity of fly ash geopolymers by using water activity sensors (HC2-AW, Rotronic) at 20, 30 and 40°C for 7 days as an effort for estimating the reaction kinetics of the geopolymers at early ages (7-days). According to the result reported as depicted in Fig. 1, the study concluded that the behavior

TABLE 1

Monitoring methods on alkali activation and geopolymerization process determined by past researches

| Researcher	Method of monitoring	Instrument and model used for interpretation	Interpretation of reaction kinetics
Hu et al. [16]	Internal relative humidity evolution	Water activity sensor	• Degree of reaction • Apparent activation energy
Peys et al. [18]	Structural evolution	X-Ray total scattering	• Contribution of iron (Fe) was determined from the extended of the scattering diagram observed.
Steins et al. [17]	Structural evolution	Small angle X-ray scattering (SAXS)	• Growth of the geopolymer is due to the aggregation of oligomers • Role of water molecule during geopolymerization observed.
Cao et al. [19]	Ultrasonic evolution	Ultrasonic monitoring system	• Changes occurred to the waves and intensity of UPV due to the reaction rate and contribution of alkali activator
Liu et al. [27]	Heat evolution	Isothermal calorimetry	• K-A-S-H nanoparticles was concluded as enhancing the reaction process due to increment of peak intensity as well as the decrement to the time taken for formation of the peaks.
Nath et al. [24]	Heat evolution	Isothermal calorimetry	• Nucleation and growth mechanism • Degree of reaction • Order of reaction kinetics • Apparent activation energy
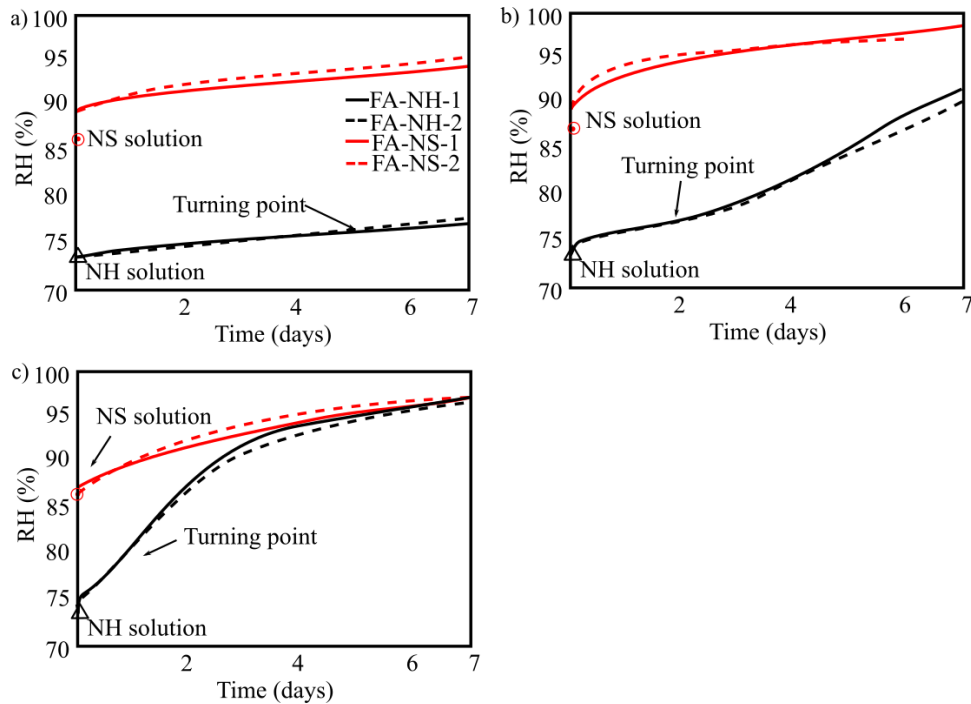
Fig. 1. Internal relative humidity evolution with different alkali activator applied (NS-NaOH+ waterglass, NH-sodium hydroxide) [16]

of humidity is different compared to ordinary Portland cement where the percentage of relative humidity gradually decreased with increasing hydration time. In addition, the study also elaborated that the changes of internal relative humidity were due to the changes in ion concentration of the pore solution which directly mirrored in the kinetics of relative humidity evolution proved in this study. The incorporation of ions such as Na^+, SiO_4^{2-}, Al^{3+}, K^+, Ca^{2+}, Mg^{2+} and OH^- for gelation and polymerization process gave a significant effect to the relative humidity.

findings, the intensity at 0.3-0.4 Å − was known to qualitatively analyze the development of pores or a layered structure in the paste as it evolved. The broad diffused peaks in this figure indicate that the changes observed during the reaction are due to slag dissolution as well as to the creation of amorphous reaction products. In addition, the prolong evolution monitored in this study is significant for determination on contribution of iron (Fe) during alkali activation process where the increment of intensity indicated the association of Fe.
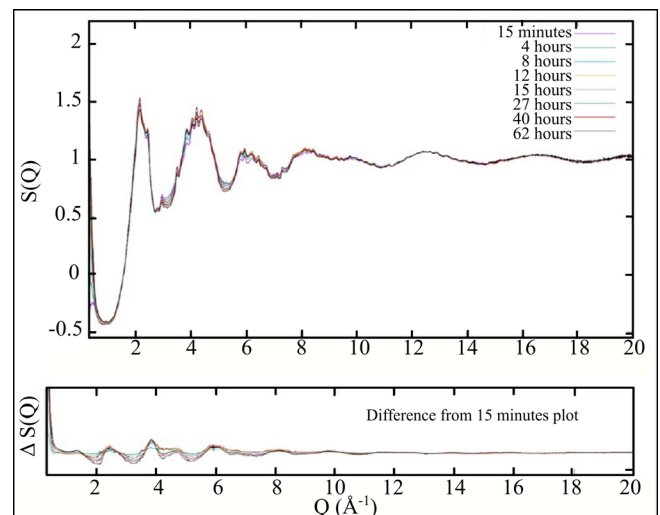
5. Structural evolution and ultrasonic evolution

Apart from monitoring the relative humidity, the structural evolution also has been monitored by past researches for monitoring the alkali activation process. For this purpose, X-ray scattering is commonly used in which can be carried out via ex-situ or in-situ. For instance, Steins et al. [17] used Small Angle X-Ray Scattering (SAXS) for monitoring the evolution of geopolymers activated by different activating solution . From the scattering pattern, the changes occurred from the SAXS diagram of scattering intensity versus scattering vector indicated the difference of resulted oligomers size from alkali activation process including the crystallinity and amorphicity of the alkali-activated materials produced.

In addition, Peys et al.[18] also utilized in-situ X-ray total scattering for monitoring the alkali activation of $CaO-FeO_X-SiO_2$ slag. Each sample was scanned in situ every 10 minutes, beginning 15 minutes after mixing and concluding 15 hours later. After these in-situ measurements, the same samples were tested again at intervals of 27 hours, 40 hours, 62 hours, and 81-hours. The result obtained was depicted as in Fig. 2. According to the

Fig. 2. Scattering diagram of alkali-activated $CaO-FeO_X-SiO_2$ slag [18]

Another effort also has been carried out for elucidating the alkali activation of slag by using embedded ultrasonic measurement. Embedded ultrasonic measurement has been considered as a useful nondestructive method and had been reported previously

for monitoring the structural changes of early cement paste [23] and the changes occurred on the waves of ultrasonic indicated the reactions occurred during hydration process. For instance, in alkali activation of slag, Cao et al. [19] utilized monitoring system where the data collection was taken artificially every minute in the first hours and then automatically every 5 min due to the simultaneous and rapid reactions of alkali activation. The ultrasonic waves of alkali-activated slag activated by sodium hydroxide can be illustrated as in Fig. 3. Stage I represents the dormant period of reaction where the reactions are noted as rapid significantly depending on the alkali activator used. Stage II depicts the acceleration period, that occurs when the UPV begins to rapidly increase due to a significant increase in the amount of reaction products and the link between the solid phases, resulting in an ultrasonic wave propagation channel from the liquid phase to the solid phase. Meanwhile, the peak started to become stagnant for 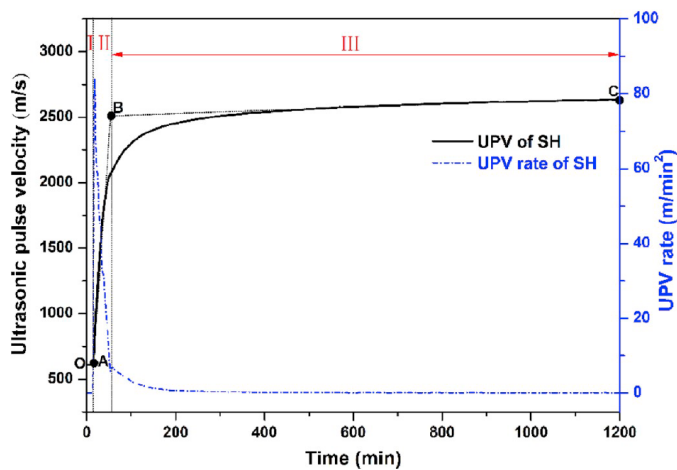Stage III as the capillary pores started to compact with reaction products. Meanwhile, utilization of sodium silicate led to additional stage (Stage IV and Stage V) which indicates the second acceleration and deceleration stage respectively due to the addition of Na_2O and SiO_2.

6. Heat evolution

Apart from water, heat is also denoted as by-products of alkali activation process. Therefore, monitoring the heat evolution of alkali activation is significant since the heat released or absorbed during the reaction process represent the chemical reactions that occurred. Numerous studies have been reported on using heat evolution to evaluate the alkali activation process including the reaction kinetics of the reactions occurred [24-26]. Similar to ultrasonic measurement, heat evolution had been used widely for monitoring heat evolution of hydration process of OPC and the peaks obtained from the calorimetric data indicates the reaction process occurred.

A study reported by Liu et al. [27] elucidates the effect of K-A-S-H nanoparticles during the alkali activation of slag. The calorimetric data represents the peaks of reactions occurred during alkali activation process in which is depicted as in Figure 4. As being elaborated by past researches [24,28], the first exothermic peak is usually the highest compared to other peak due to dissolution process and formation of monomers thus releasing heat as by-products. According to the result depicted, it was proven that addition of K-A-S-H nanoparticles increased the intensity of the peaks and the time taken formation for those peaks thus proving the enhancement in reaction rate of formation. Meanwhile, the second exothermic peak appeared to be broader and required more time of completion compared to the first exothermic peak. The intensity and broadness of the peaks were highly dependent to the addition of K-A-S-H nanoparticles.

Fig. 3. Ultrasonic pulse velocity over time for alkali activation of slag [19]
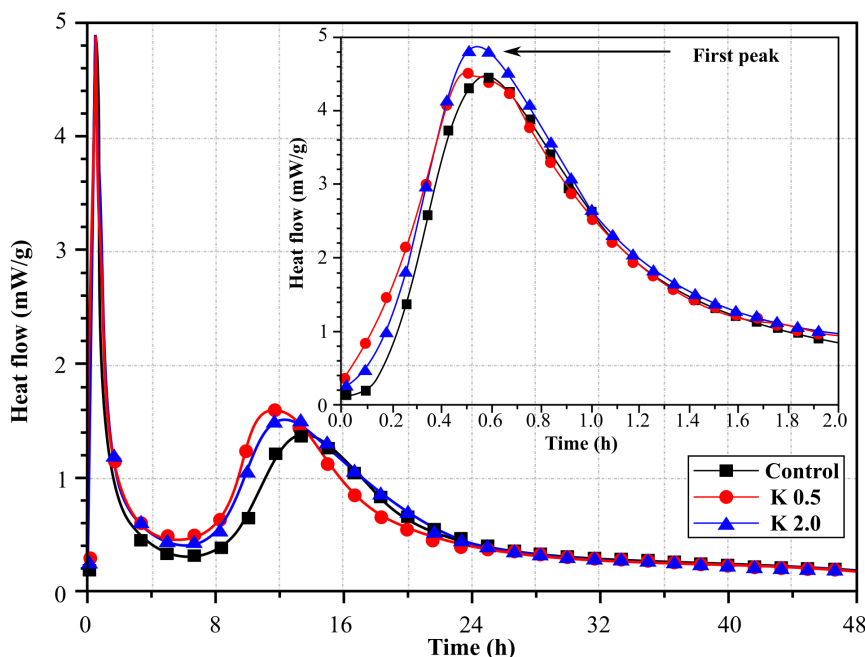

Fig. 4. Heat evolution of alkali activation of slag with incorporation of K-A-S-H nanoparticles [27]

In addition, heat evolution is commonly applied by past researches not only due to the real-time information applied, but also due to the significant changes can be observed from the calorimetric data and further used to quantify the reaction kinetics including nucleation and growth mechanism, degree of reaction [29] as well as apparent activation energy from the cumulative heat [30] evolved. Therefore, heat evolution is commonly noted as a reliable technique for elucidating the alkali activation process. The observation on the effect of parameters applied to the alkali activation can be observed through the changes in the peaks of formation and the time taken for formation of peaks.

7. Conclusions and summary of future works

From the study, it can be concluded that numerous evolution methods can be applied for monitoring the alkali activation process due to the complexity of the reactions including relative humidity, structural and ultrasonic as well as heat evolution. The significant changes occurred throughout the alkali activation process are capable to be observed via the changes in intensity or shift in the real-time data obtained thus directly represents the reactions including the dissolution and polymerization process. However, in order to emphasize the environmentally friendly and saving energy characteristics of alkali-activated materials, proper methods of evolution is highly recommended to be further explore. This is due to excessive or prolong monitoring the evolution of alkali-activated materials will lead to high energy consumption. Furthermore, the real-time information gained from those evolution techniques should be strongly correlated with the properties of the alkali-activated materials produced. This is worth to be further investigated in order to reduce the amount of time necessary for trial-and-error experimentation as well as the amount of chemicals utilized for alkali activation. Moreover, among all of these methods, heat evolution can be noted as one of interesting methods for evaluating alkali activation process. Heat evolution has been widely used method due to the ease for carried out on experimental work. Both of raw materials and liquid precursor are mixed through internal mixing or external mixing and simply put in the calorimeter for measurement. The interpretation of calorimetric data also beneficial for further used to quantify the reaction kinetics of alkali activation process including activation energy. Thus, heat evolution is worthwhile to be further explored as future work for elucidating various alkali activation process of alkali-activated materials specifically when handling with different type of aluminosilicate materials as precursors. This is due to the fact that different chemical compositions might cause different pattern of heat released and absorbed during reaction process.

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