Elucidation on Alkali Activation of Slag and Its Properties with Different Molarity of Sodium Hydroxide

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ABSTRACT

This work aims to expand on the understanding of alkali activation of slag with varied molarities of sodium hydroxide applied by using heat evolution as a real-time monitoring approach. The calorimetric data collected in this study was then utilized to examine the nucleation mechanism and growth rate of the alkali activation process. Furthermore, compressive strength, one of the important features of alkali-activated slag, was discovered to correlate with the alkali activation process. For mix designation, sodium hydroxide molarity was changed from 6M to 14M, with solid-to-liquid ratios of 0.6 and alkali activator ratios of 2.0 constant. Calorimetric data was utilized to determine reaction degree, nucleation, and growth rate mechanism using Johnson-Mehl Avrami Kolmogrov model. According to the findings, the nucleation process and growth are driven by instantaneous heterogeneous nucleation with rod-like development as the n value approaches 1. Furthermore, increasing the molarity of sodium hydroxide beyond 10M was found to reduce the total heat evolved, with the lowest being obtained when using 14M. However, the opposite observation was found for compressive strength, where further development of the strength performance was continuously rising with molarity.

Keywords: Heat evolution, nucleation mechanism, growth rate, alkali-activated slag, molarity of sodium hydroxide, compressive strength.

1. INTRODUCTION

Alkali-activated slag (AAS) has been introduced in alkali-activated materials research as one of the alternatives towards minimizing the utilization of ordinary Portland cement in construction field. Previously, ground granulated blast furnace slag (GGBFS) is extensively used as an addition in the construction area to improve the strength performance and durability properties (Krivenko *et al*., 2021; Mahmood *et al*., 2022). As a result of the promising properties generated, including strong strength performance at an early age, GGBFS is often utilized as solid precursors for alkali-activated slag (AAS). However, there is still little of information available on the underlying process of alkali activation of AAS that resulted in the excellent properties obtained, which is worth exploring. For this purpose, a real-time technique such as monitoring heat evolution can be considered. Significant changes occurred during the alkali activation process due to various influence factors such as the molarity of the alkali solution used, solid-to-liquid ratios, and alkali activator ratio, resulted in the formation of several peaks on the calorimetric data of heat evolution. The calorimetric data acquired may then be utilized to determine reaction kinetics on the alkali activation process, such as activation energy, nucleation mechanism, and growth rate. Heat evolution has been widely used for monitoring alkali activation process but most of the studies include effect of curing temperature (Nath & Kumar, 2019; Zhang *et al*., 2013) which makes it difficult for solely elucidate the effect of other influence factors at ambient condition.

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Therefore, this study intends to utilize heat evolution for elucidating the alkali activation of slag at ambient temperature of 20^{o}C as an effort on providing a better understanding on the insight mechanism of reaction process that led to enhanced properties of the alkali-activated slag produced including compressive strength performance. In this study, the effect of molarity of sodium hydroxide on the alkali activation process will be elucidated via heat evolution and its nucleation and growth rate. Additionally, significant properties of the AAS after heat evolution was evaluated specifically on the compressive strength.

2. EXPERIMENTAL PROCEDURE

2.1 Materials and Mixing Design

Ground granulated blast furnace slag (GGBFS) supplied by Macro Dimension Concrete, MDC at Chuping Plant was utilised as a solid precursor for the synthesis of alkali-activated materials in this work and will be referred to as slag throughout because no other slag was used. The characterization of slag was conducted with a particular focus on its chemical composition. X-Ray fluorescence (XRF) was used to analyse the chemical composition of slag. According to the XRF results, in terms of weight over weight percentage, the slag employed in this study is mostly made of 54.20% calcium oxide (CaO), 25.60% silicon dioxide (SiO_2), and 10.90% aluminium oxide (Al_2O_3). Furthermore, many chemical compositions smaller than 5% exist in this slag, including 0.76% iron oxide (Fe_2O_3), 3.10% magnesium oxide (MgO), 1.52% titanium dioxide (TiO_2), and 1.95% sulphur trioxide (SO_3).

For liquid precursors, a fixed ratio of 2.0:1 (w/w) of sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) was used. Prior to combining these two, the 97% purity pellet-form NaOH had to be diluted to the necessary molarities of 6M, 8M, 10M, 12M, and 14M. Meanwhile, the Na_2SiO_3 used was already in solution form. The solid-to-liquid ratio (S/L) was kept constant throughout all mixes at 0.6, while the alkali activator ratio (Na_2SiO_3/NaOH) was set at 2.0:1. Meanwhile, the molarity of sodium hydroxide was varied from 6M to 14M in this study. Alkali-activated slag (AAS) was synthesized by mixing both solid and liquid precursors at a specific mixing time (within five minutes) for each of the ratios used. After mixing, the sample was immediately employed to determine setting time and heat evolution.

2.2 Determination of Heat Evolution and Nucleation Mechanism and Growth Rate

In this work, a heat flow calorimeter built by "ToniCAL, Toni Technik" was used to monitor the heat evolution of alkali-activated slag (AAS) under isothermal conditions at a temperature of 26°C, with the goal of emphasising the ambient curing conditions. ASTM C1679-14 (ASTM Committee C09.48, 2014) and ASTM C1702 (Statements, 2014) were followed for the experiment. The external mixing approach was used in this study to homogenise the AAS mixture. This method was chosen because it resembled the mixing technique used for hardened paste testing. Given the sensitivity of the AAS properties, the mixing operation was done for a total of five minutes for each mix designation to guarantee uniform mixing duration. The heat evolution was detected during a 72-hour period, which corresponded to the measurement of the heat of hydration of Ordinary Portland Cement (OPC). Heat evolution rate (dQ/dt in J/gh) and cumulative heat evolved (Q(t) in J/g) were obtained in which was further used for nucleation and growth rate determination.

The degree of the reaction, α was determined by using Schutter method (Schutter, 1995) by using the following Equation (1).

$$\alpha = \frac{Q(t)}{Q_{max}} \quad (1)$$

Where Q (t) is the cumulative heat evolved at time t, and Qmax is the total or the maximum heat evolved to complete the reaction. Qmax can be obtained from experimental data of calorimetry.

Meanwhile, the Johnson-Mehl-Avrami-Kolmogrov (JMAK) Model, also known as Avrami's theory, was used to determine the nucleation and growth process of AAS. The JMAK's exponent(n) and k (growth rate) can be calculated using Equation (2).

$$\ln[-\ln(1-\alpha)] = \ln k + n \ln t \quad (2)$$

Equation (2) was used to plot a linear graph of y=mX + c, where y =ln[-ln(1-α)], x = ln t. The slope of the straight line represents the JMAK's exponent, n, and the y-intercept of the straight-line yields JMAK's growth rate, k. The value of n enables us to quantify the crystallization behavior of the alkali-activated slag during heat evolution.

2.3 Compressive Strength Determination

The leftover fresh paste of alkali-activated slag with different molarities of sodium hydroxide from heat evolution determination were moulded in 50mmx50mmx50mm moulds and cured in an ambient temperature at 1-day and 3-day ages for compressive strength determination. Compressive strength testing was performed in accordance with ASTM C109 utilising a Shimadzu Japan UH-1000 kNI Universal Testing Machine (UTM).

3. RESULTS AND DISCUSSION

3.1 Heat Evolution Analysis

As being illustrated in Figure 1, only one noticeable peak observed for all molarity of sodium hydroxide (NaOH) applied of the calorimetric data. In general, increasing the molarity changed the appearance of the peak significantly. The intensity of the peak increased as the molarity of sodium hydroxide (NaOH) increased from 6M to 10M, with the maximum at 10M (99.15 J/gh). This is consistent with previous study that stated raising the molarity of NaOH produces an increase in heat flow owing to the quick reaction process known as wetting and dissolving of alkali activation (Cornelis *et al.*, 2018; Nmiri *et al.*, 2017). Alkali-activated slag heat flow decreased with molarity increments of 12M and 14M, with the lowest intensity (41.41 J/gh) at 14M. In addition, 12M and 14M peak formations are wider than 6M, 8M, and 10M. With more OH- ions in the alkali-activated slag system, more monomers produced, which increased hydration and polymerization and created more AAS gels, hindering heat flow. This explained the wide development and small right shift of the 12M and 14M peaks. The total cumulative heat evolved started to decrease at 12M and 14M (324 J/g and 320 J/g, respectively), confirming that AAS gel formation was hindered by increasing.

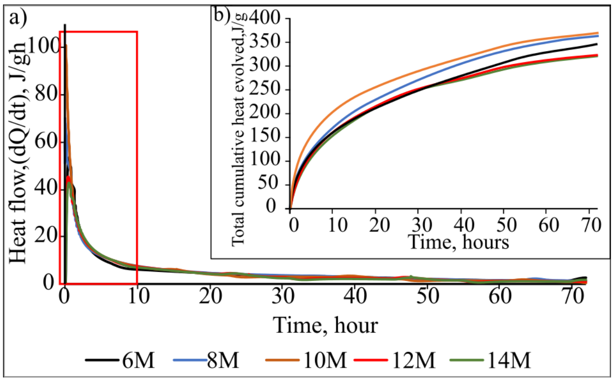

Figure 1. Heat evolution and total cumulative heat evolved.

3.2 Nucleation Mechanism and Growth Rate Analysis

The degree of reaction of alkali activation slag with different molarities of sodium hydroxide used in this investigation, and the results are illustrated in Figure 3. Increasing the molarity up to 10M caused a quick reaction within 10 hours, with the largest reaction at 10M (0.58) and the least at 6M (0.42). Another interesting observation was that 12M and 14M molarities had a greater degree of reaction than 6M (0.48 and 0.55, respectively) despite low heat flow during the first 10 hours. This showed that increasing sodium hydroxide molarity increases reaction rate, notably during alkali activation's early stages of wetting, dissolving, and hydration.

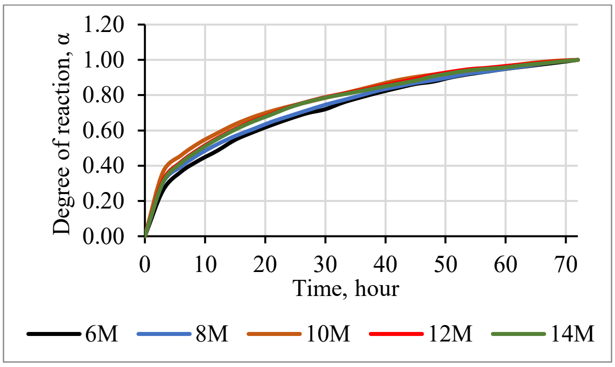

Figure 2. Degree of reaction.

Meanwhile, the nucleation mechanism and growth rate of alkali-activated slag (AAS) was extracted from a straight-line graph in which can be illustrated and summarized as in Figure 4 and Table 1 respectively. Figure 4 and Table 1 show that the JMAK exponent, n, ranges from 0.8348 to 0.8992, and the intercept of the graphs yields k values from 0.0917 to 0.1398. The n values greater than 0.5 and approaching n=1 indicate that the nucleation growth process of AAS is the same regardless of the molarity of sodium hydroxide used. According to the n values, the nucleation mechanism of alkali activation of slag in this study is governed by an instantaneous nucleation mechanism (one dimensional) with a rod-like growth, also known as needle-like growth. The n values smaller than one observed can be attributed to a decrease in the development rate of radial nuclei as a result of the inhibition of already created nuclei, as well as a decrease in molecular mobility (Siyal *et al.*, 2016). In addition, Growth rate (k) is inversely proportional to n. The rising values of k, which indicate alkali activation growth rate, showed that increasing sodium hydroxide molarity enhanced growth rate and OH- ion availability for dissolving, producing more monomers for nucleation and polymerization.

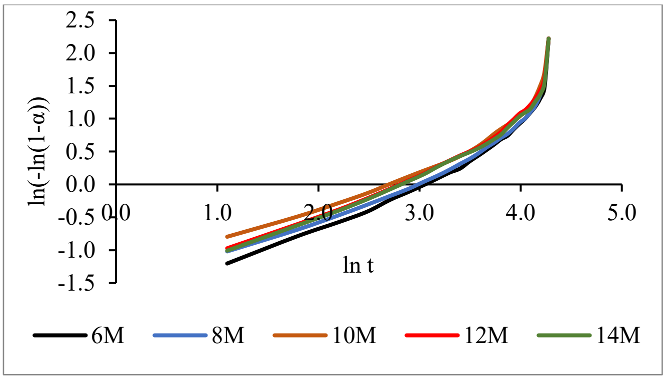

Figure 3. JMAK Model of nucleation mechanism and growth rate.

Table 1 Extraction of JMAK exponent and growth rate from JMAK Model

Molarity	$Y = mX + C$	**Avrami exponent (n)**	**Growth rate (k)/min^{-1}**
6M	Y=0.8426X - 2.3595	0.8426	0.0917
8M	Y= 0.8844X- 2.2601	0.8844	0.1029
10M	Y= 0.8992X -2.0759	0.8992	0.1032
12M	Y= 0.8460X -2.2694	0.8460	0.1136
14M	Y= 0.8348X- 2.2601	0.8348	0.1398

3.3 Compressive Strength Analysis

The compressive strength was tested at 1-day and 3-day ages to study the strength growth during the course of heat evolution, and the results are shown in Figure 5. In general, increasing the molarity of NaOH resulted in increased compressive strength of the AAS. However, the delayed rise of AAS strength might be related to the S/L ratio of 0.6, which involved more liquid precursor than solid. For 1-day age, regardless of the maximum total cumulative heat developed at 10M, 14M (12.09 MPa) had the highest compressive strength and 6M (5.97 MPa) had the lowest compressive strength. This is based on the rapid formation of the AAS polymeric network in the presence of high concentration of hydroxide ions (OH-), which results in high strength performance. Further growth of AAS gels occurred throughout the heat evolution, as indicated by the increment of compressive strength at 3-day age, which was the increment of approximately 50% of compressive strength at 1-day age, The highest compressive strength was observed at 14M (15.95 MPa). This may be the result of the rearrangement and reorganization of the AAS polymeric backbone into a structure that is more stable, which in turn resulted to an increase in compressive strength.

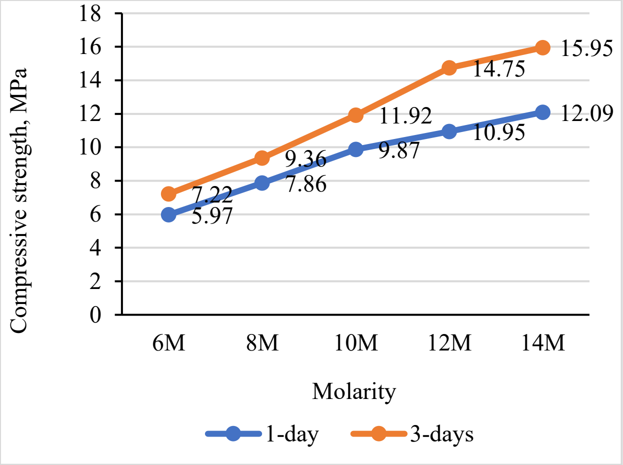

Figure 4. Compressive strength of alkali-activated slag.

4. CONCLUSION

In summary, heat evolution determination is an important signal for understanding the alkali activation process of alkali-activated slag. According to real-time monitoring, increasing sodium hydroxide molarity increases total cumulative heat evolved and peak heat evolution intensity. However, it was revealed that increasing the molarity (over 10M) reduces both the total cumulative heat evolved and the maximum intensity of the heat evolution peak due to the heat flow in the system being delayed. Furthermore, the nucleation and growth mechanism analysis revealed that, regardless of the molarity of sodium hydroxide used, the nucleation mechanism of alkali activation of slag was governed by an instantaneous nucleation mechanism (one dimensional) with a rod-like growth, also known as needle-like growth, as the JMAK exponent (n values) obtained. Meanwhile, the JMAK plot growth rate demonstrated that increasing the molarity of sodium hydroxide greatly increased the growth rate of the reaction during the first 10 hours of the reaction process, as evidenced by the degree of reaction results obtained. Meanwhile, as evidenced by compressive strength, it has been proven that the highest total cumulative heat developed does not represent the better strength performance of the alkali-activated slag, as continuous strength development was found when molarity was increased.

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