Kinetics of geopolymer’s solidification: Effect of concentrations and curing temperatures

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Abstract. This paper report the experimental study on the kinetic of geopolymer’s solidification by determining setting time by varying activator concentrations of 10 M, 12 M, 14 M and 16 M, and curing temperatures of 30, 60, 80 and 100°C. However prior to the study of the effect the feasibility of equipment using Vicat Needle. The transformation process of geopolymer crystal formation is analyzed by Avrami’s kinetic theory. From the results of the experimental showed the increase activator concentration and curing temperature produce shorter setting time for geopolymer’s solidification. From the Avrami kinetic theory’s the growth form of crystal in the geopolymerization showed constant (K) of particle growth is 5.42 x 10⁻² and the value of Avrami’s component n = 2.310 so that it can be concluded from the perspective of Avrami’s kinetic theory, the rate of crystal growth solidification in this geopolymerization process shows a two-dimensional structure.

1. Introduction

The solidification method in this study is the geopolymer process produced by reaction of aluminosilicate solids contained in fly ash material with strong base activators producing binders/adhesives such as cement. Factors that influence the properties of geopolymers, namely the type and concentration of activator, activator modulus, curing temperature, curing time, and the ratio of alkaline solution in solids. The results of previous studies indicate that each of the above factors in the right amount becomes a parameter to produce geopolymer concrete/paving blocks with high compressive strength [1,2].

Study the effect of the concentration of alkali solution on the compressive strength in fly ash as a geopolymer concrete base material [3]. It was reported that the higher the concentration of alkali solution affected the increase in compressive strength, the researchers stated that the strength of the geopolymer material is very dependent on the concentration of alkaline solution, in addition to decreasing compressive strength when the ratio of water to solid geopolymers increases. Paver blocks geopolymer from fly ash with variations of NaOH 8 to 12 M activator concentration, the compressive strength increased with increasing the concentration of activator [4].

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From the researchers described above there are more physical and chemical properties of geopolymers after the solidification process such as compressive strength, acid resistance, porosity and geopolymer absorption, while the study before the geopolymer solidification process still a few, therefore in this experimental studying the effect of parameters concentration and temperature in the solidification phase in the geopolymerization process and analysis from the perspective of Avrami’s kinetic theory. This study also studied the Vicat Needle tool in determining geopolymer solidification and its correlation with Avrami’s kinetics theory of crystalline transformation from nucleation phase to crystal growth.

2. Materials and methods

2.1. Materials

Materials used in this research, fly ash from PT. RAPP Pelalawan Riau province, Sodium Hydroxide (NaOH) solution from Basic Chemical Labor Department of Chemical Engineering FT-UR, Sodium Silicate (Na$_2$SiO$_3$) in the form of a solution from PT. Sinar Sakti Kimia Solo, fine/sand aggregate from Rimbo Panjang Quarry Kampar Regency, Riau. The equipments used is the scale, measuring cup, stopwatch, piknometer, oven and Vicat Needle in the Materials Technology laboratory of the Department of Civil Engineering FT-UR.

2.2. Preparation

The kinetics of geopolymer solidification reactions: Preparation of NaOH solutions concentrations of 10, 12, 14, and 16 M. Then the activator solutions of NaOH and Na$_2$SiO$_3$ were mixed with a ratio of 1:2. Then fly ash : activator solution (NaOH + Na$_2$SiO$_3$) with a ratio of 1:3 mixed with variations in concentration NaOH, after that the molding process with temperature variations of 30, 60, 80, and 100 °C.

2.3. Rate of Test

The solidification rate test with the Vicat Needle tool and note the solidification rate for each concentration. As addition in this experimental the highest compressive strength at 14 M NaOH [5]. Explanation and analysis of results obtained using Avrami’s Kinetic Theory.

3. Result and Discussion

3.1. Effect of Temperatures

From the experimental results, variations in concentration and curing temperatures which results in shorter time for each increase in temperature at a fixed concentration and vice versa each variation in concentration at a fixed temperature against the geopolymer solidification process. Furthermore, from the Kinetic Avrami’s Theory, the form of crystal growth in the geopolymerization process shows a two-dimensional structure while certain samples from geopolymers show secondary nucleation in geopolymer growth. Temperature variation to the rate of solidification. As seen In Figure 1 the relationship between temperature variation on the geopolymer solidification rate at a concentration of 14 M NaOH. Samples
with a temperature of 80°C reach the fastest maximum hardening compared to samples with temperatures of 100, 60°C and room temperature. This can be seen from the time it takes the sample temperature of 80 °C for 35 minutes, temperature of 100 °C for 40 minutes, While the temperature of 60 °C and T. room is equal to 60 minutes. This is due to the rate of evaporation of water faster with increasing time. At temperatures of 80 and 100 °C the rate of evaporation of water is faster than the temperature of 60°C and room temperature, but at a temperature of 100 °C the geopolymer product is cracked so that it affects the compressive strength obtained. The best results in this study occurred at an optimum temperature of 80 °C where the geopolymer product did not crack (cracking) with the highest compressive strength.

![Figure 1](image1.png)

**Figure 1.** Variation in temperature to the rate of solidification in 14 M NaOH.

The increase in curing temperature will accelerate the geopolymerization process due to the reduced water content in the geopolymer material which has an effect on compressive strength [6]. The geopolymer compressive strength is very dependent on the pore size during the geopolymerization process is influenced by the higher temperature the number of pores of the geopolymer material is getting smaller, the optimum temperature is obtained at 80°C [7].

![Figure 2](image2.png)

**Figure 2.** Effect variation in temperature to Avrami’s Plot.
As seen Figure 2. The effect of temperature at the optimum concentration NaOH 14 M on geopolymer solidification. From the Avrami plot of the temperature effects of the Avrami exponent value (n) and the growth rate constant (K) formulated and tabulated in Table 2. Based on Table 2. above it can be seen that the value of Avrami’s exponents varies in all temperature variations tested. The value (n) starts from 0.959 to 2.529 where the smallest n is at room temperature while the largest (n) value is located at 100 °C. The Avrami’s value of this exponent is very important to determine the form of geopolymer growth. Then for the fastest crystal growth rate (K) occurs at a temperature of 80 °C. If the value of n = 1, indicates growth of the nucleus occurs instantly, while the value of n = 2 - 3 growth spherulit and sporadic nucleation forms. The value (n) between 0.959 and 2.529 shows growth in instantaneous nucleation and two-dimensional growth nucleation [8]. However, for the geopolymer growth the expected exponent value starts from 1-2 in two-dimensional shape. These results indicate that the growth of geopolymer forms can be said to be two dimensions.

Table 2. Avrami’s Exponent for Temperatur 14 M NaOH.

| Temperature (°C) | Avrami Exponent (n) | Growth Rate (K), (min⁻¹) |
|------------------|---------------------|--------------------------|
| T.room           | 0.959               | 4.76 x 10⁻⁵              |
| 60               | 1.066               | 4.45 x 10⁻⁴              |
| 80               | 2.310               | 4.75 x 10⁻²              |
| 100              | 2.529               | 1.56 x 10⁻²              |

3.2. Effect of Concentrations

As seen in figure 3 the relationship between concentration variation on the geopolymer solidification rate at temperature 80°C. Samples with concentration NaOH 14 M reach the fastest maximum hardening compared to samples concentration 16 M, 12 M and 10 M. This can be seen from the time it takes the sample 14 M for 35 minutes, 16 M for 45 minutes, While the others equal to 60 minutes. The amount of dissolution is largely depending on the concentration of NaOH and curing time. Thus, increase the concentrations will increase the number of OH⁻ ion in the solution for leaching process that lead to acceleration of the geopolymerization process. However based on the literature review, when the
concentration of NaOH solution in higher than 15 M, the dissolution supposed to be decreasing due to increase in coagulation of silica [9]. In short the higher molarity of NaOH concentrations lead to geopolymerization process which the reducing the setting time of geopolymer. As seen figure 4 it shown the results for the effect of different activator concentrations on geopolymer compaction. From the Avrami’s plot, exponent value (n) and the growth rate constant (K) are formulated and tabulated in Table 3.

![Figure 4. Effect variation in concentration to Avrami’s Plot.](image)

| Koncentration (M) | Avrami’s Exponent (n) | Growth Rate (K) (min^{-1}) |
|------------------|-----------------------|---------------------------|
| 10               | 1.993                 | 7.16 x 10^{-4}            |
| 12               | 1.397                 | 1.08 x 10^{-2}            |
| 14               | 1.608                 | 5.42 x 10^{-2}            |
| 16               | 0.938                 | 4.33 x 10^{-2}            |

As seen Table 3, that the value of the Avrami’s Exponent varies in all variations of the concentration tested. The value (n) starts from 0.938 to 1.993 where the smallest is at the concentration of activator 16 M, while the largest (n) value lies in the concentration of activator 10 M. Avrami value of this exponent is very important to determine the form of geopolymer growth. Then for the fastest crystal growth rate (K) occurs at a concentration of activator 14 M is 5.42 x 10^{-2}. From the results obtained both temperature and concentration variations obtained the same optimum value at 14 M NaOH concentration and 80°C temperature. The value (n) of the variation in concentration between 0.938 and 1.993(2.0) shows growth in instantaneous nucleation and two-dimensional growth nucleation[10,11]. However, for geopolymer growth the expected exponent values start from 1 - 2 in two-dimensional form. These results indicate that the growth of geopolymer forms can be said to be two dimensions.

4. Conclusion
From the results and discussion described, it can be concluded that the geopolymer paving blocks produced are: The highest kinetics constant of particle growth (K) reaction with a value of 5.42 x 10^{-2} and the value of Avrami’s component n = 2.310 obtained at the optimum temperature of 80°C in
14 M NaOH activator concentration. The Avrami’s Exponent value range for all samples ranged from 0.959 to 2.529 so it can be concluded that the form of geopolymer growth has 2-dimensional disc structure.

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